CERTIFICATE OF TRANSLATION

January 7, 2009

I, Angela Christie, hereby certify that I am competent in both English and German languages.

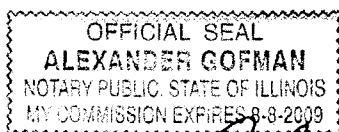*I further certify that under penalty of perjury translation of the aforementioned document:*
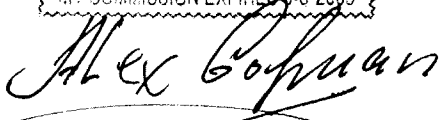
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from the German language into the English language is accurate and correct to the best of my knowledge and proficiency.

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The following information is an excerpt of the documentation submitted by the inventor.

㋚ Electric Component and Method of its Fabrication

㋝ The invention pertains to an electric component with a layer, which contains at least one polymer and which influences the electrical properties of the electric component. The characteristic feature of the invention is that the polymer contains at least one molecular organic semiconductor and that the at least one molecular organic semiconductor exhibits at least one polymerizable group by means of which the molecular organic semiconductor is polymerized to the polymer.

Description

[0001] The invention pertains to an electric component with a layer affecting the electrical properties of the electric component and containing at least one polymer.

[0002] Electric components of this type are known from the state of the art. The paper by P. Ingleby et al. "Effect of micro-electrode geometry on response of thin-film poly(pyrrol) and poly(aniline) chemoresistive sensors" in Sensors and Actuators, B57(1999) 17-27 already indicates a chemoresistive sensor containing a pyrrol- or aniline-based polymer to influence the electrical properties of the component.

[0003] It is the objective of this invention to improve a component of the above type, and to make available a method for its fabrication.

[0004] This objective is met for a component of the above type by the electric component according to claim 1. The invention also provides a method for the manufacture of the component described in the invention according to claim 18.

[0005] The invention has in particular the advantage that due to the introduction of a molecular organic semiconductor the electric properties of the polymer film can be selectively changed. In the following, molecular organic semiconductors shall be understood to be groups of molecules, which in their pure state function as organic semiconductors. Polymers created by polymerization of organic semiconductors like phthalocyanine are already known from US Patent 5,120,610; however, these polymers do not provide the additional modification of the molecular organic semiconductors with at least one polymerized group as is the case in this invention. However, this modification of the molecular organic semiconductor with at least one polymerizable group allows in a particularly advantageous way the very precise adjustment of the electrical properties of the thusly equipped component. For example, if the component is a sensor, it is possible that by choosing a specific molecular organic semiconductor – for example phthalocyanine – and by targeted modification of this molecular organic semiconductor, the properties of such polymers can be adjusted with the help of a polymerizable group – aniline, for example – such that the active sensor layer created by the polymer is sensitive to light of a specific wavelength while not being sensitive to another. This may serve as a sample only. Depending on the choice of the molecular organic semiconductor and the polymerized group, the invention furthermore allows the user to adjust the sensitivity of the polymer for a particular solvent, so that the relevant component will be sensitive to this solvent only while nearly insensitive to all other solvents.

[0006] The invention also provides an electric component, which, due to its innovative polymer layer, can be adjusted to specific application requirements in a new and innovative way not known before. The advantages of the invention shall be listed here as part of the introduction. In the following description of the invention, a number of additional advantageous embodiments of the invention based on its design, its properties and its advantages will be explained in greater detail.

[0007] In a preferred embodiment of the invention, the at least one molecular organic semiconductor contains one macrocyclic ligand and/or the ligand's metal complexes, in particular substituted and/or unsubstituted phthalocyanine, substituted and/or unsubstituted porphyrines, substituted and/or unsubstituted porphyrazines, substituted and/or unsubstituted naphtalocyanines, substituted and/or unsubstituted biphtalocyanines, and/or substituted and/or unsubstituted chlorines, or a precipitated aromatic, in particular substituted and/or unsubstituted perylene dyes and pigments and their derivatives, substituted and/or unsubstituted terryfenes and their derivatives, substituted and/or unsubstituted quaterrylenes and their derivatives, and/or substituted and/or unsubstituted coronenes and/or their derivatives. It is furthermore possible to use dyes, which as pure substances exhibit semiconductor properties, like substituted and/or unsubstituted merocyanines. In an highly preferred embodiment, the quoted merocyanines are used as coating for CD's. Such coating utilizes the characteristic of merocyanines to change their absorption response in the presence of laser beams of a specific wavelength.

[0008] Especially preferred are cases where the at least one molecular organic semiconductor contains at least one element of a multitude of elements including phthalocyanine, hemiporphyrazine, triazolhemiporphyrazine, biphthalocyanine, naphthalocyanine, phorphyrine, perylene, perylene dicarbonic acid anhydride, perylene dicarbonic acid imide, perylenetetracarbonic acid dianhydride, perylene tetracarbonic acid diimide, perylene tetracarbonic acid-monoanhydride monoimide, corones, coron dicarbonic acid hydride, corone dicarbonic acid imide, corone tetra carbonic acid dianhydride, corone tetra carbonic acid diimide, corone tetra carbonic acid monoanhydride monoimide, rubicen, rubicen dicarbonic acid anhydride, rubicen dicarbonic acid imide, rubicen tetracarbonic acid dianhydride, rubicen tetracarbonic acid diimide, rubicen tetracarbonic acid monoanhydride monoimide, imidazole, imidazole carbonic acid anhydride, imidazole dicarbonic acid imide, imidazole tetra carbonic acid dianhydride, imidazole tetracarbonic acid diimide, and imidazole tetracarbonic acid monoanhydride monoimide. These organic semiconductors have shown to be especially advantageous embodiments since they are easy to manufacture and to process, and allow the defined adjustment of specific properties of a polymer of this design. Of course, any other molecular organic semiconductors can be used for the inventive purpose as well. The manufacture and properties of some of the previously listed molecular organic semiconductors will be described in greater detail further below.

[0009] In order to completely understand the inventive molecular organic semiconductors mentioned above, these molecular organic semiconductors will be compared to inorganic semiconductors and conductors. The synthesis and the properties of preferred molecular organic semiconductors of this invention are described as well.

[0010] As introduction, we shall have a look at the electrical properties of metals as well as inorganic and organic semiconductors. For this purpose, **Fig.** 45 shows an overview over the conductivities of organic

and inorganic conductors and semiconductors. In addition, the following Table 1 shows the mobility and conductivity of silicon (Si), an inorganic semiconductor, and of PcCu, an organic semiconductor, each in the undoped state. The table also indicates the spacing between the atoms or molecules in each crystal lattice.

Table 1

	$a_{spec}[S/cm]$	$\mu \ [cm \cdot V^{-1} \cdot s^{-1}]$	Lattice Spacing [nm]
Si	10^{-6}	1000	0.23
PcCu	10^{-14}	3.5	0.4

[0011] Compared to inorganic semiconductors, organic semiconductors exhibit a distinctly lower conductivity. According to the traditional classification they would be considered insulators ($\sigma_{spec} < 1(T^{10}$ S/cm). They do, however, exhibit the following characteristics typical for semiconductors:

- Conductivity increases with temperature;
- Conductivity increases in the presence of foreign substances (e.g. when doped);
- They have a thermoelectric voltage;
- Photoconductivity;
- Depletion and enrichment boundary layers in contacts —▶ photovoltaic activity;
- electrochemical activity;
   a) active as electrochromic layer, charge storage device
   b) as catalyst for electrochemical transformations
   - photo-electrochemical activity (photo voltages, photo currents in contact with electrolytes).

[0012] Characteristic samples of organic semiconductors are large-surface, π-electron-rich aromatic compounds like phorphyrines, perylenes, and phthalocyanines. These compounds have the advantage that they are easy to manufacture in large quantities and with great purity. Phthalocyanines, for example, can be created with a purity of 10^{14} to 10^{16} traps per cm^3. In addition, these classes of compounds are also thermally and chemically very stable and only oxidizing acids can corrode them. Furthermore, they exhibit an intensive absorption characteristics in the visible range, with extinction coefficients, which in solution may be up to 10 cm mol. In contrast to inorganic semiconductors, which are covalently linked in the crystal bond, the inorganic molecules are held in crystal bonds only by Van der Waals interactions. The spaces between the individual atoms are accordingly larger. The splitting of the molecule orbitals into broad bands (valence and conductive band) as is the case in inorganic semiconductors, advantageously does not occur in organic semiconductors due to the low interactions. Therefore, molecules maintain the properties of the individual molecules also in the solid-state bond. The conductive carriers in organic semiconductors are generally significantly less mobile than in inorganic semiconductors. The band model, which is used to explain the conductivity mechanism in inorganic semiconductors, plays a secondary role for the transport of charges in organic semiconductors. In organic crystals, the transport of the charge carriers is explained mainly by hopping mechanisms, like the so-called "Phonon-assisted Hopping" and through activated tunnel processes.

[0013] In comparison, conductive polymers, due to their conductivity in doped condition (conductive polymers will be discussed later in greater detail), may also be called electrical conductors or metals ($\sigma_{spec} > 10$ S/cm). Their conductivity decreases as the temperature increases, just like in inorganic metals. These materials do not exhibit any field effects or thermoelectric voltages. Here, the mechanism of the charge transport, just like for organic semiconductors, cannot be described by the classic band model. The charges are transported via so-called mid-gap states, which are generated by the presence of solitons. Typical conductive polymers are therefore polypyrrol, polyaniline, polyphenylenvenylidene and polyacetylene, i.e. polymers exhibiting a conjugating system along the polymer chain, and which are explained in greater detail below. The synthesis and the properties of such polymers are also described in greater detail below. Conductive polymers advantageously cover a broad range of specific conductivities. This conductivity strongly depends on the doping of the polymer. The doping can therefore be used advantageously for the enhancement of the inventive properties of the components. With little doping, the conductive polymers act like organic semiconductors. In the undoped state they can be considered insulators due to their low conductivity.

[0014] Following is a description of advantageous embodiments of the inventive molecular organic semiconductors based on their synthesis and their properties. There are direct references to the attached drawing in order to facilitate the understanding of these preferred embodiments.

[0015] Let's begin with a description of the synthesis and the properties of phthalocyanines, which may be advantageously utilized for the invention. Phthalocyanine can be prepared with or without a central metal. In the state of the art, more than 70 different central metals have been covered for phthalocyanines with a central metal.

Furthermore, in the state of the art, the basic structure of phthalocyanine has been substituted with symmetrical and asymmetrical substituents. Metal-free phthalocyanine, i.e. without central metal, can be made of metal-containing phthalocyanines whose central metals, like Ca and Li, are labile to acids. Metal-free phthalocyanine can also be synthesized directly from 1,3-di-iminoiso-indolenine 1 in high-boiling solvents. Synthesis from 1,2-phthalacid-nitril2 in pentanol with DBU as catalyst is gentler and provides a higher yield. **Fig.** 1 provides an overview over the methods of the synthesis of metal-free phthalocyanine.

[0016] **Fig.** 2 presents preparation methods for the synthesis of metal-containing phthalocyanines. Not every method can be used for substituted dinitriles. Phthalocyanine can be synthesized with 1,2-cyanbenzoe-acid-amide 3 and phthalacid-nitrile 4 as reactants. Additional options to synthesize phthalocyanine are based on phthalacid-anhydride 5, on 1,2-bromobenzene 6, on 1-bromo-2-cyanbenzene 7, and on phthalacid-imide 8. The synthesis methods for phthalocyanines without central metals are also suitable for the synthesis of metal-containing phthalocyanines.

[0017] Phthalocyanines occur in different crystal structure modifications. The three most important modifications are called α, ß, and X. Vapor-depositing a phthalocyaninato-zinc in vacuum onto a substrate results in the α-modification, at a substrate temperature between 50°C and 140°C. When the layer is heated to over 210°C the α-modification changes into the ß-modification. Cooling the place of recrystallization, however, creates amorphous films.

[0018] **Fig.** 3 shows the exact bonding angle in the molecule crystal on the sample of zinc-phthalocyanine. The different modifications also differ in their conductivity and their UV-Vis-spectrums. Decisive is therefore the modification of the prepared thin film.

[0019] Also described as advantageous embodiments of the inventive molecular, organic semiconductor are the synthesis and the properties of perylene and perylene derivatives.

[0020] When 3,4,9,10-perylene-tetra-carbonic-acid is heated, 3,4,9,10-perylene-tetra-carbonic-acid-dianhydride (in the following called PTCDA) is synthesized. PTCDA can be used as starting product for the synthesis of 3,4,9,10-perylene-tetra-carbonic-acid-diimide (in the following called PTCDI). PTCDI's can be advantageously used for the invention since they are easily accessible and can be purified well through sublimation or chromatography. The absorption maximums of the monomer imides in the solution in the UV-Vis-spectrum differ very little. The maximum absorption point is also very little affected by the solvent being used. The bands are at 525 nm, 489 nm, and 458 nm. The fluorescence spectrums with a band at 540 nm and 575 nm concur for different dyes within 5 nm. Symmetric PTCDI's can be synthesized by heating the PTCDA with an amine and a water-eliminating agent (e.g. Zn-acetate) in high-boiling solvents (e.g. quinoline). However, only thermally stable amines can be used for this synthesis method. Amines with easily separable second substituent at the alkyl or aryl moiety, like carbonic, sulfonic or sulfuric acid groups can be brought to reaction only under mild conditions. PTCDA can be converted with glycine in a DMSO/H$_2$0 mixture at 100°C. In this manner, a uniform product is available after about three hours. **Fig.** 4 shows a schematic view of the synthesis of symmetric perylenes.

[0021] Let me now briefly explain the synthesis and the properties of phorphyrines as additional preferred molecular organic semiconductors. Contrary to phthalocyanines and perylenes, phorphyrines occur in nature. They fulfill important biochemical functions in animals and plants. For example, they form the prostatic group in hemoglobin and myoglobin, and are therefore responsible for the transport of oxygen in the blood. In cytochromes, they play a decisive role in the transport of electrons. Phorphyrines are synthesized by way of cyclocondensation of pyrrol derivatives with aldehydes, preferably in an acidic environment. The transformation of pyrrol with formaldehyde to unsubstituted porphine supplies small yields. In contrast, transformation with substituted aldehydes, which leads to meso-substituted porphirines, delivers higher yields. **Fig.** 5 shows the reaction scheme of the Rothermund reaction in the sample of 5,10,15,20-Tetrakis(p-phenyl-carbonic-acid-)porphirines. In the reaction shown in **Fig.** 5 the central metal ion must be inserted later.

[0022] Another preferred embodiment of the invention is characterized by the fact that the group can be polymerized via electropolymerization. In this embodiment, electropolymerization can be used for the polymerization and the deposition of the polymer onto the substrate of an electric component, for example.

[0023] The groups themselves contain in preferred embodiments at least one element from the multitude of aniline, pyrrol, thiophene, ethylene, indole, paraphenylene, aminoanthracene, aminoaphthaline, aminophenol, carbazole, benzoquinone, acrylnitrile, pyrrolidones, phenylendiamine, tetrathiapentales, acrylic acid and phenols and their derivatives and substituents. The modification of the polymerizable groups for the modification of the molecular organic semiconductors will be described in greater detail further below. **Figs.** 37-44 show for purposes of clarification the structures of aminophenol (**Fig.** 37), aminoanthracene (**Fig.** 38), aminoaphthaline (**Fig.** 39), acrylic acid (**Fig.** 40), tetrathiapentalene (**Fig.** 41), carbazole (**Fig.** 42) pyrrol (**Fig.** 43), phenol (**Fig.** 44). When bonding these polymerizable groups to the molecular organic semiconductors it is preferred for these groups not to be attached directly to the molecular organic semiconductors but only indirectly via an intermediate molecule chain, a so-called spacer. This spacer preferably includes a molecule chain containing at least one element from the multitude of $(CH_2)_n$, $(CFH)_n$, $(CF_2)_n$, $OCO(CH_2)_n$, $OCO(CF_2)_n$, $OCO(CFH)_n$, $COO(CH_2)_n$, $COO(CF_2)_n$, $COO(CHF)_n$, $NH(CH_2)_n$, $NH(CF_2)_n$, and $NH(CHF)_n$ wherein n = 0 to 20.

[0024] Another preferred embodiment is characterized in that the polymer is electrically conductive. Conductive polymers are derivatives of polyenes, i.e. compounds with large conjugated systems. Due to oxidation or reduction processes, they exhibit excess charges and can also be considered polymer salts. **Figs.** 6a to 6d show idealized chain

structures of the polymers polyacetylene (**Fig.** 6a), polyvinylides (**Fig.** 6b), polypyrrol (**Fig.** 6c), and Polyaniline (**Fig.** 6d). The actual polymerization generates cross-links and branches. Pyrrols even create ring-structures. Polyaniline and Polypyrrol can be polymerized from their monomers, aniline and pyrrol, chemically as well as electrochemically. The electrochemical polymerization occurs for both polymers at the anode. Hydrogen peroxide and ferric (III) chloride can be used as initiators for the chemical synthesis. Polyacetylene and polyvinylidene, however, can only be chemically polymerized. Acetylene is polymerized on cooled substrates using Ziegler-Natter catalysts. Polyvinylidene is created from benzene with the help of a mixture of an oxidation agent and a Friedel-Crafts catalyst (CuCl/AlCl₃). The high electric conductivities are generated by mobile positive and negative charge carriers (so-called solitons), which are a result of doping. The material can be doped electrochemically during the synthesis of the polymers or afterwards by treating the polymers with oxidation or reduction agents.

[0025] The inventive combination of the above-named conductive polymers and components of molecular organic semiconductors results advantageously in a combination of their individual properties. Due to the inventive polymerization of the molecular organic semiconductors via the above-mentioned electro-polymerized groups, initially the conductivity of the materials created in this way is especially increased. The inventive molecular organic semiconductors also form redox-active centers for the catalysis, the electro-catalysis and the sensorics of the inventive electric components in the conductive matrix of the conductive polymers. In doing so, the polymers have the advantage that, as heterogeneous catalysts, they can be separated from each reaction mixture. Especially the inventive combinations of porphyrines and conductive polymers also offer options for electron transfer processes.

[0026] Following is a discussion of additional preferred embodiments of the invention regarding the polymerizable groups based on a sample. Also discussed is the synthesis and the properties of the monomers formed with the help of the polymerizable groups and the molecular organic semiconductors for the creation of the polymer in the inventive component. These preferred embodiments of the inventive component and/or the method for the manufacture of the inventive component will also be described in the following based on the figures in the drawings.

[0027] First, let's look at the synthesis of the monomers. Of interest in this context are pyrrol-substituted phthalocyanines as p-conductive monomers, where the polymerizable group is located above the spacer in order to minimize the steric hindrance during the polymerization by the phthalocyanine. The synthesis concept should include the option of pyrrol-substituted phthalocyanine synthesis with different spacer lengths in order to determine during the production if the reactivity of the monomers increases with spacer length. The electrical properties of the polymers also change when the phthalocyanines as conjugated systems are separated by longer aliphatic spacers from the pyrrols. Among others, the invention included the synthesis of pyrrol-1-yl-alkanol. The N-alkylated compounds have the advantage that they can be easily be made synthetically, and the length of the alkyl group can be easily varied. As functional group, the hydroxyl group offers options for a connection to the phthalocyanine. Generally, the connection to the phthalocyanine can be brought about by two types of synthesis. One option is the insertion of the desired substituent during the synthesis. This is often done by way of synthesis of an accordingly substituted phthalonitrile. 4-nitro-phthalonitrile is a suitable starting substance since the nitro-group can be nucleophilly substituted by aliphatic hydroxyl groups. The other option to introduce the electro-polymerizable group is a substitution on phthalocyanines. Here, the esterification of a tetrakis-4-carboxy-phenoxy-phthalocyanine is preferred. This concept has the advantage that the polymerizable group is not present throughout the entire synthesis process as reactive group on the molecule. Tetrakis-4-carboxy-phenoxy-phthalocyanine, however, is less soluble in organic solvents, so that a direct esterification in organic solvents is not possible. In esterifications via acid chloride is has been shown that the transformation does not occur quantitatively on all substituents. The synthesis via 4-nitro-phthalonitrile was therefore preferred since it delivers clean, quad-substituted phthalocyanines.

[0028] The synthesis described in reference to this embodiment can be broken down into four steps:

- Synthesis of pyrrol-1-yl-alkanols
- Preparation of the dinitriles
- Cyclotetramerization
- Insertion of the central metal ions.

[0029] The pyrrol-1-yl-alkanol can be synthesized from pyrrolyl potassium and the necessary bromo-alkanol by nucelophile substitution in DMSO/THF. With 71%, this reaction had the highest yield for the manufacture of the pyrrol-1-yl-alkanols. A schematic view of the reaction is shown in **Fig.** 7. The alcohol being used is in protolysis equilibrium which, due to the lower pKs-value of 2-bromoethanol is fully on its side. Therefore, twice the molar concentration of pyrrolyl potassium, in relation to the alcohol, is used. The result is a product mixture of pyrrol and the desired pyrrol-1-yl-alkanol. The required column-chromatographic purification is relatively time-consuming. In addition, the test series performed by the inventors still indicated contaminations in the product. For the invention, it is therefore preferred to synthesize the desired pyrrol-1-yl-alkanols according to a slightly modified recipe. In doing so, the preparation of pyrrolyl potassium is dropped. Instead, potassium-t-butylate is added for deprotonation. In this reaction, the pyrrolyl potassium is generated in situ. The pyrrol excess is not needed for this reaction so that pyrrol-1-alkanol is created as the only monomer. In addition, the crown ether as phase transfer catalyst can be added, allowing the reaction to occur successfully in low-boiling solvents as well.

In this preferred variation, the material is purified by distillation in oil pump vacuum with a Vigreux column. This embodiment of the inventive synthesis method – as the synthesis explained above – also resulted in a product mixture. Also determined in both described syntheses was a reaction of the unprotected hydroxyl'group to ether under the given alkaline conditions with bromo-alkanol, which was still present.

[0030] Further preferred for the synthesis of the monomers according to this invention is therefore the synthesis method schematically shown in **Fig.** 8. In this synthesis from pyrrol-1-yl-alkanol, the amino-alkanol is first esterified with acetic acid before the dimethoxytetrahydrofuran is added. The amino group substitutes the oxygen in the dimethoxytetrahydrofuran, and the metoxy groups are thermally eliminated at higher temperatures, thus creating the ethyl acetate of the pyrrol-1-yl-alkanol. The ethyl acetate is then split into methanol by adding KOH. Purification is performed by distillation in oil pump vacuum via a Vigreux column. The raw product yield is about 70%. One advantage of this synthesis method is the trouble-free processing of large batches. This formulation can easily be used for n=2.

[0031] It has been shown that the pure product yield is – due to the high losses during distillation – dependent on the size of the batch. The above explained formulation should be varied for n=3 and n=5. In this case, the formulation calls for 2-hydroxyethylamine to be used four times in excess of the dimethoxytetrahydrofuran. Since this is a liquid, it can be easily added in the form of drops. 3-hydroxypropylamine is a high-viscosity liquid, and 5-hydroxypenthylamine is a solid. To add the liquid in drops, 3-hydroxypropylamine was mixed with 30 ml n-propanol and 5-hydroxypethylamine was solved in n-propanol. For economical reasons, both amines should be used in small excess only (x 1.3 or x 1.5) It was furthermore determined that in the case of longer-chain alcohols the saponification after stirring over night does not complete. For this reason, the process should preferably be varied prior to saponification. In order to separate the acetic acid from the acetic acid CO-pyrrol-1-yl-alcylylester as completely as possible, the combined organic phases are washed three times with a saturated solution of potassiumhydrogencarbonate. The reaction time of the subsequent saponification is set to 20 hours. The yields are, independently of chain length, between 25% and 60%.

[0032] The synthesis of 4-(2-pyrrol-1-yl-ethoxy)-phthalonitrile and the 4-(3-pyrrol-1-yl-propoxy)-phthalnitrile takes place according to the principle schematically shown in **Fig.** 9. This representation indicates a nucleophile substitution in the aromatic compound. Due to the M-effect of the cyano groups, the electron density at the C_4-position in the aromatic compound is decreased. Nitro functions are good leaving groups and can therefore be substituted with hydroxyl groups. In this substitution reaction, aromatic hydroxyl groups shows the highest reactivity. In aliphatic hydroxyl groups, the reactivity decreases as the length of the chain increases. The ratio of the reactants (educts) is modified to facilitate the processing. In the described synthesis, the alcohol and the nitrophthalonitrile are used with a molar ratio of 1:1. In order to ensure the complete transformation of the nitrophthalonitrile, the alcohol is used at an excess of at least 1.3, so that the chromatographic separation of the nitrophthalonitriles is advantageously not needed. In the synthesis of 4-(3-pyrrol-1-yl-propoxy)-phthalnitrile, the reaction time is additionally increased by 4d. In both cases, the raw products precipitate only after careful neutralization. In acidic solution, the pyrrol starts to polymerize which leads to significant yield losses, so that acidification should be avoided. The crystals form only in ice-cold solution or after complete separation from contaminants. 4-(3-pyrrol-1-yl-propoxy)-phthalonitrile has a crystallization time of about 4 weeks. For the preferred embodiment of the inventive synthesis method described herein it is therefore preferred to continue to use product in the form of oil when the MS and NMR spectrums are free of contaminants. The yield decreases with increasing chain length.

[0033] The cyclotetramerization to 2,9,16,23-tetrakis-(pyrrol-1-yl-alkoxy)-phthalocyanine is performed according to the synthesis shown schematically in **Fig.** 10. In this case, 0.2 g-0.5 g dinitrile are solved under nitrogen in boiling pentanol. A spatula tip of lithium is added and stirred for 45 minutes. The synthesis has shown that the yield increases when the reaction time is lengthened to one hour. After the reaction, the pentanol is first completely removed in the vacuum, and the remaining oil is given for precipitation into a methanol/water-mixture (volume ratio 1:1). In the case of tetrakis-(pyrrol-1-yl-alkoxy)-phthalocyanine, lithium as central metal is removed by washing with the methanol/water mixture. In order to remove the lithium in the tetrakis-(pyrrol-1-yl-alkoxy)-phthalocyanine, the phthalocyanine is stirred in a pH 5 buffer, then filtered and neutralized with water. Treatment with acetic acid is not recommended since this leads to a high loss due to polymerization. For the synthesis of the phthalocyanines containing central metals, the specifications are modified. The metalization is performed without the processing in pentanol by adding the necessary metal salt to the batch of the cyclotetramerization. UV-Vis-spectroscopy is used for product control. It turned out that zinc and cobalt generate strong interactions with the complex. Nickel, on the other hand, can be extracted from the phthalocyanine by repeated washing with water. For this reason, the product is not processed with the methanol/water mixture but in pure methanol. The attainable yields are way over 80%.

[0034] In the case of the perylenes, n-conductors are preferred as base structures which – depending on the choice of the polymerizable group – can be polymerized at the anode or at the cathode. The preferred n-conductive molecular organic semiconductor is 3,4,9,10-perylene-tetracarbodiimide. The polymerizing groups should be attached such that they do not affect the conjugating system, so that the character of the conductivity is not changed. Since a knot is located at the nitrogen of the diimide in the HOMO and LUMO, any moieties at this location do not affect the electronic properties of the system. Hydroxyphenyl substituent is preferred because it is cathodically polymerizable. Chosen as anodically polymerizable group is an aminophenyl substituent.

[0035] The syntheses can be broken down as follows:

- Synthesis of 1,6,7,12-tetrachloro-3,4,9,10-perylene-tetra-carbonic-acid-anhydrid
- Synthesis of the perylene-3,4,9,10-tetra-carbodiimides from diamino compounds

- Synthesis of the perylene-3,4,9,10-tetra-carbonic-acid-diimide from mono-amino compound, wherein the synthesis of the Perylen-3,4,9,10-tetracarbodiimides and the 1,6,7,12-Tetrachloro-3,4,9,10-perylenetetracarbodiimides follow the same synthesis formulation.

[0036] The 1,6,7,12-tetrachloro-3,4,9,10-perylenetetra-carbonic-acid-anhydride is synthesized according to the formulation schematically shown in **Fig.** 11, through chlorination of the anhydride. Chlorosulfonic acid can be used to insert chlorine into aromatics. In this reaction, iodine acts as the catalyst. The transformation has a yield of 98%.

[0037] The synthesis of the perylene-3,4,9,10-tetracarbodiimides and the 1,6,7,12-tetrachloro-3,4,9,10-perylene-tetracarbodiimides are performed as shown in **Fig.** 12. In this formulation, the diamino component is used in excess of over 10 times to lower the chance of polycondensation. Furthermore, it should preferably be made sure to avoid carcinogenic solvents. For example, toluene or xylol can be used instead of benzene if this is possible due to the solubility of the reactants. Despite the high excess of the diamino component, perylene-tetra-carbonic-acid dianhydride cannot be completely transformed. Boiling in potassium hydroxide allows the anhydride groups of this compound to be transformed into two groups of carbonic acids. The resulting perylene-tetra-carbonic acid is soluble in potassium hydroxide and can thus be separated. The resulting products are soluble in formic acid and could thus be separated from the generated polymers. The products can also be created from the appropriate mono-amino-nitro-compounds by way of a two-step synthesis, where in the first reaction step the perylene carbodiimides are synthesized and the nitro groups are reduced in the second step.

[0038] According to **Fig.** 13, perylene-3,4,9,10-tetra-carbonic-acid-diimide can be synthesized from mono-amino compounds. For X = H, the transformation is quantitative, for X = Cl, the yield is 20%. The reactivity of the perylene 3,4,9,10-tetra-carbonic-acid-diimide is significantly reduced through the introduction of chlorine atoms. An inhibition of the reactivity due to the chlorine atoms during the reaction with diamino components does not occur.

[0039] In the following, I will now address additional details of the inventive electropolymerization of the phthalocyanines. In order to minimize the number of educts (reactants) for the electropolymerization, a single-compartment cell with a volume of 5 ml will be used, which contains a 1 x 1 cm working electrode made of ITO (Indium-Titanium-Oxide), a platinum net as counter electrode, and a silver wire are reference electrode. The silver wire functions as quasi-reference electrode and should be calibrated against ferrocene after each measurement. When Hg/HgCl or Ag/AgCl are used as reference electrode, traces of water may get into the solvent. Since small amounts of contaminants or traces of water may intercept the radicals generated at the anode and inhibit the polymerization, no direct reference electrode should be used. Two different precipitation methods can be used: potentiostatic precipitation or potentiodynamic precipitation. In the potentiostatic precipitation, a constant potential is applied between the reference electrode and the working electrode, while during potentiodynamic precipitation a cyclically changing potential is used. Another precipitation method is the reaction at a constant flow of current (galvanostatic) or specified varying current flow (galvanodynamic). The polymerization conditions should be optimized for a maximum achievable layer thickness for the potentiostatic as well as for the potentiodynamic precipitation. In addition to the pyrrol-substituted phthalocyanines, the inventors also used tetraminophthalocyaninato-nickel as reference (comparison) substance. Due to the low solubility of the monomers ($3 \cdot 10^{-4}$ to $9 \cdot 10^{-4}$ mol/l), work with a saturated solution is recommended. To make sure that the solution maintains the same concentration throughout the entire reaction time, about 10^{-3} mol/l each should be used. The voltages shown in the cyclovoltamograms in the Figures are in reference to SCE.

[0040] In the cyclovoltammetry triangular voltages are applied between the operating and the reference electrode with the use of a potentiostat. In doing so, the potential between a starting potential and a return potential is continually changed over time. The currents flowing between the working electrode and the counter electrode are measured. The current densities are determined by dividing the currents through the active electrode size. Cyclovoltammograms are representations of the currents or current densities resulting from this measuring method plotted in relation to the voltage. Reaction 1 shows a cyclovoltammogram of a substance which, in solution, can enter into the following reaction:

$$A \xrightleftharpoons[\text{-e}^-]{\text{e}^-} A^-$$
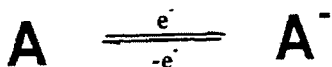
[0041] The charges Q absorbed or released by the electrode are determined by integration of the curve:
$q = \int i \, dt$ Equation 1

[0042] Cyclovoltammetry differentiates between three boundaries:

- the reversible reaction
- the quasi-reversible reaction
- the irreversible reaction.

[0043] In the reversible reaction, the difference between the cathodic and the anodic peak potential is between 57 and 60 mV. The theoretically calculated value of 59.2 mV is rarely measured since resistance effects of the solution cause small distortions. The charge values of q_A und q_K are the same. The peak potential is calculated with the following formula:

$$\lnot E^0 = \frac{E_{pc} + E_{pa}}{2}$$

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Equation # 2

[0044] If the rate of the electron transfer is slow in comparison to the time (at high feed rates), the thermodynamic equilibrium between A and A' is disturbed. The difference between the peak potentials increases. In this case, the redox potential cannot be determined exactly anymore. This is called a quasi-reversible reaction. Equation 2 is usually used for an approximation of the redox potential.

[0045] When the peaks of the anodic and the cathodic reaction do not overlap anymore, we speak in the electro-chemical sense of an irreversible reaction. The shown cyclovoltammograms are not irreversible reactions in the electrochemical sense, they are irreversible due to their chemical nature. For these reactions, no redox potentials can be determined.

[0046] The Figures in the drawing show the changes of the cyclovoltammograms during the potentiodynamic polymerization. The resulting layer thicknesses and the absorbed charges will be discussed afterwards in comparison to the potentiostatic polymerizations. For each monomer, two cyclovoltammograms (CV) are shown. The first CV according to **Fig.** 14 indicates the first five cycles in order to illustrate the changes of the potential between monomer and polymer. In the second CV according to **Fig.** 15 every fifth cycle is plotted to show the saturation of the currents. The individual polymerization parameters are optimized prior to that. The potentiodynamic electropolymerizations shown here take place at a feed rate of 10 mV/s. An increase in the scanning speed leads to less pronounced oxidation and reduction peaks and smaller film thicknesses after the same precipitation time. Solvents are acetonitrile, dichlormethane (DCM), and dimethylformamide (DMF). The pyrrol-substituted phthalocyanines achieve from DCM the highest layer thicknesses, and the tetra-amino-phthalocyaninato-nickel from DMF. Conducting salts investigated are tetrabutylaminoniumtetrafluorophorate (TBABF$_4$), tetrabutylamoniumperchlorad (TBACIO$_4$), and tetrabutylamoniumhexafluorophosphate (TBAPF$_6$), wherein optimum precipitation of the tetraaminophthalocyaninato-nickel results from a solution with 0.1 mol/l TBACIO$_4$. In contrast, the pyrrol-substituted phthalocyanines reach the highest layer thicknesses at a precipitation of 0.1 mol/l TBAPF$_6$. The potentiodynamic polymerization is stopped after two hours. The following table shall provide an overview of the optimized reaction conditions as described in the invention:

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Table 2

Monomer	Monomer Initial Weight 10^{-3} mol/l	Solvent (5 ml)	Conducting Salt	Cond. Salt Initial Weight (0.1 mol/l)	Polymer-zation Time
NiPc-[NH$_2$]$_4$	3.2 mg	DMF	TBAClO$_4$	0.16 g	2 hrs
H$_2$Pc[pyr-rolylpro-poxy]$_4$	5.0 mg	DCM	TBAPF$_6$	0.19 g	2 hrs
H$_2$Pc[pyr-rolylet-hoxy]$_4$	4.8 mg	DCM	TBAPF$_6$	0.19 g	2 hrs
ZnPc[pyr-rolyl-ethoxy]$_4$	5.1 mg	DCM	TBAPF$_6$	0.19 g	2 hrs
NiPc[pyr-rolylet-hoxy]$_4$	5.0 mg	DCM	TBAPF$_6$	0.19 g	2 hrs
CoPc[pyr-rolylet-hoxy]$_4$	5.0 mg	DCM	TBAPF$_6$	0.19 g	2 hrs

[0047] The potentiodynamic electropolymerization of tetra-aminophthalocyaninato-nickel is performed in DMF with 0,1 mol TBAClO$_4$ as conducting salt. The monomer has three oxidation peaks (0.29 V; 0.72 V; 0.98 V) and two reduction peaks (0.55 V; 0.95 V). The position of the oxidation peaks shifts during the transition from the monomer to the oligomer clearly to more positive potentials. The first oxidation peak of the oligomer occurs at 0.55 V and the second at 0.95 V. The third oxidation peak of the oligomer occurs outside the driven voltage range. The second reduction peak does not shift (0.87 V). In contrast, the first reduction peak of the oligomer is slightly shifted to higher voltages of 0.35 V.

[0048] In **Fig.** 15, every fifth cycle has been recorded. As can be seen, the intensity of the oxidation and reduction peaks first increases and then decreases, starting with the 20th cycle. The potentiodynamic electropolimerization of tetrakis-(2-pyrrol-l-yl-etoxy)-phthalocyanine is performed in DCM as solvent. Conducting salt is 0.1 mol/l TBAPF$_6$. **Fig.** 16 shows the corresponding CV. The tetrakis-(2-pyrrol-l-yl-etoxy)-phthalocyanine without a central metal has two oxidation peaks (0.79 V; 1.20 V) and one reduction peak (1.03 V). The position of the reduction peak does not change during the polymerization. During the transition from monomer to oligomer the oxidation peaks shift to more positive potentials (1.2 V; 1.38 V). The oxidation peaks and reduction peaks strongly decrease after the first five cycles. The maximum current density at 1.4 V continuously decreases as the thickness of the layer increases.

[0049] In regard to electropolymerization it should be noted that electropolymerization belongs to the group of electro-organic syntheses. Electron-rich aromatics can be brought to polymerization via electrochemical oxidation or reduction. Most conductive polymers are polimerized anodically (oxidatively). This method can also be applied advantageously to non-conductive polymers. The cathodic polymerization from phenol to poly-phenylidenoxide is also possible. The advantage of this method are the resulting homogeneous layers, whose thickness can be well controlled throughout the precipitation time. Advantageously, this technique also allows the doping

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of the layers already during the separation.

[0050] It may potentially be possible to perform a radical polymerization using current to generate radicals on modified electrodes.

[0051] According to a sample embodiment, the preparation takes place in a 3-electrode configuration as is used for cyclovoltammetry. As an alternative, a 2-electrode configuration could be used as well. **Fig.** 17 shows the schematic outline of a configuration pursuant to the invention. In this process, a silver wire or a silver wire with a silver chloride coating is used as quasi-reference electrode (RE). It has the advantage that it is not required to be in contact with the hydrous electrolytes; therefore contaminants in the form of traces of water can excluded. It must, however, be calibrated against ferrocene after each measurement. For electro-organic syntheses, 1- and 2-compartment cells will be used. The configuration according to Fig. 17 is a 2-compartment cell. In this cell the anode (AE) is separated from the cathode (GE) by a semi-permeable partition (ST). For the invention it has proven to be advantageous to configure the electrodes in a specific way. Normally, the reference electrode is located closely to the working electrode, while the counter electrode is located further away. For the invention, however, it is preferred for the counter electrode to be positioned rather closely to the working electrode and for the reference electrode to be positioned behind the working electrode at a greater distance. The suitability of the cell depends on the monomer and should be individually adjusted to the monomer.

[0052] The cell shown in **Fig.** 17 has two additional openings for the flushing of inert gases. In order to reach the homogeneous layers, the counter electrode (GE) should have the same geometry and size as the working electrode, and should be aligned in parallel. The precipitation can take place according to three different procedures: at a constant voltage (potentiostatic precipitation), at a constant current (galvano-static precipitation), or at a cyclically varying potential (potentiodynamic precipitation). The type of precipitation then determines the morphology of the layers precipitated in this way. Potentiodynamic precipitation, for example, creates layer with a higher porosity, i.e. larger pores. In this way, the sensitivity of such layer will be improved because a more gas molecules of a gas to be detected can diffuse into a more porous layer. The operating mode of the indicated cell shall be explained on the sample of pyrrol. The individual steps of the reaction are shown in **Figs.** 18a to d. In the first step, pyrrol is oxidized at the anode into a radical. This radical can then either react with another radical or with a pyrrol molecule. The first case shall here be called radical-radical-dimerization, while the second case shall here be called radical-substrate-dimerization, wherein the first reaction channel is more likely. In both cases two protons are split off, and during the radical-substrate coupling one electron is released. The result of the progressing reaction is polypyrrol. The electropolymerization of aniline and amino-substituted aromatics shall be explained on the sample of the electropolymerization of tetraaminophthalocyaninatonickel as indicated in **Fig.** 19. The mechanism of the electropolymerization of tetraaminophthalocyaninatonickel shown in **Fig.** 19 is also an anodic polymerization. In this reaction as well, radical-radical-dimerization is more likely.

[0053] In the following, the potentiodynamic and the potentiostatic precipitation will be compared to each other.

[0054] First, we compare the number of charges absorbed during the static and the dynamic polymerization of P2. In order to calculate the charge amount of the potentiostatically precipitated polymers, the polymerization is aborted after different reaction times, and the currents measured during the reaction are integrated over time. In order to determine the charge amounts during the potentiodynamic polymerization, a CV recorded over a time period of 2 hrs is broken down into its individual cycles. Then, using the feed rate, the voltages are converted into times. The resulting graphs (current over time) are integrated to calculate the charges that were absorbed and released in each cycle. The results are subtracted in order to obtain the number of charges left behind inside the polymer. For a comparison of the potentiostatic and the potentiodynamic electropolymerization, the total amounts of charges per cycle are determined by adding each previous cycle and plotted over time up to each cycle.

[0055] The results of the calculation are shown in **Fig.** 20. In the same polymerization time the potentiodynamically created layers of the tetrakis-(2-pyrrol-l-yl-phthalocyanine) pick up 1/3 more charge carriers than the potentiostatically created layer. The charge picked up by the polymer saturates with increasing reaction time in both preparation methods. The following table shall provide a comparison between potentiostatic and potentiodynamic electropolymerization.

Table 3

Monomer	Polymerization Method	Layer Thickness [nm]	Porosity [nm]	Absorbed Charges [C]
NiPc-[NH$_2$]$_4$A1	static	690	60	0.228
	dynamic	1100	380	0.503
H$_2$Pc[pyrro-lylpro-poxy]$_4$P1	static	5050	1270	0.232
	dynamic	2850	600	0.342
H$_2$Pc[pyrro-ly-lethoxy]$_4$P2	static	3000	1200	0.181

	dynamic	1900	400	0.298
ZnPc[pyrroly-lethoxy]$_4$P3	static	120	30	0.024
	dynamic	120	10	0.020
NiPc[pyrroly-lethoxy]$_4$P4	static	80	60	0.049
	dynamic	100	20	0.097
CoPc[pyrro-lyl-ethoxy]$_4$P5	static	810	60	0.021
	dynamic	740	200	0.020

[0056] In polymers reaching a layer thickness of more than 1 μm, the charge absorbed with potentiodynamic precipitation is significantly greater than with potentiostatic precipitation. The thicknesses of the layers of the polymer phthalocyanines with nickel as central metal are greater with potentiodynamic electropolymerization. In other polymer films containing a central metal, the achieved layer thicknesses are similar after both preparation methods. Of the films of polymers without a central metal, the potentiostatically precipitated films reach greater thicknesses. For the invention, layer thicknesses between 1 μm and 5 μm are advantageous.

[0057] The monomers, with very thin layers, use less charges. However, the charge consumption per layer thickness is different for each monomer. The maximum layer thickness clearly depends on the structure of the monomer. In the pyrrol-substituted phthalocyanines the monomers without a central metal grow clearly to greater layer thicknesses.

Increasing the length of the alkyl spacer between the phthalocyanine and the pyrrol substituent leads to greater layer thicknesses after the electropolymerization. The integration of the central metal in these compounds leads to smaller layer thicknesses in the same polymerization time. The following parameters are the main reasons for the different layer thicknesses:

- Solubility
- Reactivity
- Conductivity of the resulting polymer
- Electrode kinetics

[0058] The pyrrol-substituted phthalocyanines containing a central metal have a lower solubility than those without a central metal ($\sim 10^{-4}$: $\sim 5 \times 10^{-4}$). This explains why the layers of the central-metal-containing monomers are thinner. However, it does not explain why the cobalt-containing phthalocyanine achieves greater layer thicknesses than the phthalocyanine containing zinc or nickel. The reason is that the redox-active central metal activates the polymerization. The polymerization behavior of the pyrrol-substituted phthalocyanines differs from the behavior of the tetra-amino-substituted phthalocyanines. Of the pyrrol-substituted phthalocyanines, the cobalt-containing one reaches the greatest layer thicknesses, followed by the nickel-containing phthalocyanine. The zinc-containing monomer grows the least. In the tetra-amino-substituted phthalocyanines, the nickel-containing phthalocyanine grows the thickest layers, the zinc-containing phthalocyanine grows the second-thickest layers, and the cobalt-containing shows the lowest reactivity. Phthalocyanines containing nickel exhibit higher conductivities than other phthalocyanines. This is the explanation of the thick layer growth. Cause for the different reaction response is the electron density of the radical cat-ions. The tetra-amino-substituted phthalocyanines have due to the mesomer-pushing amino groups a higher electron density in the aromatic compound than the pyrrol-substituted phthalocyanines.

[0059] The monomer with the C3-spacer between the pyrrol group and the phthalocyanine grows in a thicker layer than the monomer with the C2-spacer. Since the solubilities are about the same, this reason is excluded for the different grow response. The low steric hindrance of the pyrrol group in the monomer with the C3-spacer increases the reactivity of the polymerization. The conductivity of the resulting polymers is similar.

[0060] The polymer of the amino-substituted phthalocyanine has a significantly greater conductivity than the pyrrol-substituted phthalocyanines.

[0061] The electrode kinetics for the monomers described herein are similar since the size of the molecules and their polarity don't vary much. One may also assume that the diffusion constants and the interactions with the electrode are similar as well.

[0062] The electropolymerization is performed on the synthesized perylenes. In the presence of negative potentials, the hydroxy-phenoxy-substituted perylene 16 can be precipitated with CaCl as conducting salt from DMF on ITO. An electropolymerization in the presence of TBAPF$_6$ as conducting salt is not possible. Conspicuous is the redox pair at -0.56 V. Since it does not occur in the electro-polymerizable phthalocyanines, it can be classified as part of the perylene base structure. The maximum shifts to less negative potentials. The growing polymer is harder to reduce than the monomer. In **Fig.** 21, every fifth cycle of the electropolymerization has been recorded.

[0063] The tetra-chlorinated hydroxyphenoxy-substituted perylene 17 precipitates under the same conditions only in very thin layers. The redox pair of the perylene base structure is located at 0.3V and is only recognizable during the first cycles. **Fig.** 22 also shows every fifth cycle of the potentiodynamic deposition. The current densities decrease rapidly after a few cycles.

[0064] The aminophenoxy-substituted perylenes I1-I5 cannot be deposited in DMF on ITO neither with CaCl$_2$ nor with TBAPF$_6$ as conducting salt. In contrast, in platinum electrodes, the polymerization of the perylenes sets in with di-amino-phenylether as substituent (I1, I2) with TBAPF$_6$ as conducting salt. The films, however, grow only to a very low thickness. **Fig.** 23 shows every fifth cycle of the potentiodynamic electropolymerization of I1.

[0065] Here, too, the introduction of the chlorine atoms proves unfavorable for the electropolymerization. As can be obtained from **Fig.** 24, the current densities in the potentiodynamic deposition of the chlorinated PTCDI I2 clearly lower than those of the non-chlorinated derivative I1. The decrease of the current densities with the number of cycles is significantly greater for the chlorinated PTCDI derivative.

[0066] Generally, the PTCDA that are converted with di-amino-diphenylether (I1, I2) show the highest reactivity among the amino-substituted perylenes I1-I5. The steric hindrance can therefore be reduced during the electropolymerization by a longer spacer. The increased electron density in the attacking aromatic due to the oxygen as hetero-atom promotes the polymerization additionally. The substitution of the PTCDA with methyl-paradia-minodiphyl (I3) does not lead to an increase in reactivity. The steric hindrance during the electropolymerization is in this case also reduced but the electron density in the reacting aromatic is not increased. There is no difference in reactivity between the meta- and para-di-aminophenyl-substituted PTCDA's (I4 and I5).

[0067] The polymerization parameters should be optimized for the p-di-amino-substituted PTCDA (I4). By adding perchloric acid as catalyst, the reactivity of the electropolymerization can be increased. The potentiodynamic deposition of I4 on ITO is successful. **Fig.** 25 shows every fifth cycle of the electropolymerization of I4 in DMF with TBAPF$_6$ as conducting salt with two drops of perchloric acid as catalyst. The reaction starts at the more positive potentials in comparison to NiPc[NH$_2$]4A1 (1.4 V for I4 and 1.1 V for NiPC[NH$_2$]$_4$A1), whereby the maximums of the oxidation and the reduction for PTCDI I4 shifts to the less positive potentials. One reason for the shift in potential is the protonation of I4.

[0068] Since the electropolymerization is catalyzed by acids, the general use of acidic electrolytes during the reaction is recommended. The use of anhydrous acids like HBF$_4$-etherate complexes also leads to an additional reactivity increase.

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[0069] Another preferred embodiment of the inventive component includes a preferably electrically conductive substrate which, further preferably, may be micro-designed in the form of interdigital electrodes. Onto this substrate, the layer containing the polymer is preferably polymerized. The digital electrodes are preferably designed as fingers, which may also be interlaced like combs that are facing each other. Preferred is a spacing between the digital electrodes of one comb of between 1 μm and 2 μm. A small distance between the digital electrodes is advantageous because the polymer film applied afterwards can in any case be applied as one closed layer.

[0070] In another embodiment of the invention, the electrodes of the inventive components can be modified by electrodepositing of another, additional metal. In doing so, only one part of the electrodes of the inventive component can be modified by electrodepositing another metal, so that two or more are made available on the inventive component in different micro-structures. The polymer film can afterwards be polymerized on these different electrodes. In doing so, a heterogeneous polymer film, as described below, can also be used in order to match the properties of the inventive component to a gas that is to be detected.

[0071] In another preferred embodiment of the invention, the component is a sensor to measure at least the presence, preferably the concentration of gases and/or liquids and/or solids, preferably of gases in air, wherein the layer to measure the presence, preferably the concentration, is sensor-active. The inventively designed layer thus forms the central part of a sensor. Such sensors can also be used as arrays, i.e. in series, for the quantitative and qualitative detection of gases and/or liquids. These sensors cab be used for unspecific measurements for air quality control in a motor vehicle, for the sensor-controlled ventilation of closed rooms, e.g. bathrooms, and for food quality checks, for example in produce and meat departments and warehouses. The inventive polymer sensor is able to advantageously simultaneously capture multiple different gases produced by the ripening process of food items. In doing so, it is possible to integrate different polymers into one single polymer film, so that the properties of the sensor can be matched to the food items to be detected and monitored. But also only one polymer is able to capture different gases since the polymer also reacts differently with different gases. These different reactions can afterwards in a CPU be compared to specific calibration values of the applicable gases, so that these gases can be determined by comparing the measured values to the calibration values.

[0072] In additional preferred embodiment, the layer or film, which according to the invention contains a combination of a polymer and a molecular organic semiconductor, may also be an antistatic film, an organic field effect transistor (OFET), an organic light-emitting diode (LED), a photovoltaic cell, a Schottky-cell and/or a battery. Some of these applications are explained below.

[0073] The largest industrial application of conductive polymers is the electromagnetic shielding of electronic components. Antistatic film are mostly manufactured from poly-3,4-ethylendioxythiophene (PEDOT).

[0074] Another production-ready application are OLED's. **Fig.** 26 shows the schematic structure.

[0075] A reactive metal like calcium or magnesium is used as cathode. Typical organic deposits for light or emitting layers are PPV's or Alq$_3$. In OLED's, PEDOT is used to smooth the substrate and as hole-conductor-layer. Indium-Tin-Oxide (ITO) is a typical anode material. It is highly conductive and transparent. However, conductive polymers can be used as well to produce flexible OLED's. The operating principle is identical to that of inorganic LED's. Holes are injected through the anode, electrons are injected through the cathode. Both migrate through the applied field into the light-emitting layer, where they recombine while releasing electromagnetic radiation.

[0076] OLED's are the physical reverse of the photovoltaic cell, in which current is generated in response to electromagnetic radiation. For organic photovoltaic cells, an organic n-semiconductor (e.g. Me-PTCDI) and an organic p-semiconductor (e.g. ZnPc) are combined. It is also possible to create Schottky cells from an organic semiconductor and a conductive polymer as metal replacement. **Fig.** 27 shows typical structures of an organic photovoltaic cell and a Schottky cell.

[0077] While the life cycles and the light intensities of organic light-emitting diodes can compete with inorganic LED's, organic photovoltaic cells do not achieve the efficiency of inorganic cells. The efficiency is 1% (MePTCDI/ZnPc) in comparison to 35.8% (GaAs/GaSb). **Fig.** 28 shows the operating principle of a photovoltaic cell.

[0078] In the depletion layer, which is created by the contact of an n-semiconductor and a p-semiconductor, electrons are excited by electromagnetic radiation from the occupied state into the unoccupied state. The resulting exciton pair is separated by the electric field. Another potential application of organic semiconductors and conductive polymers is the architecture of OFET's. The principle of operation is identical to that of inorganic field effect transistors. The currents between the emitter and the collector can be controlled by a voltage applied to the base. Contrary to inorganic transistors, their field of application is not limited to the amplification of currents but also extends into chemical sensorics. The semiconductor properties of organic materials change in response to interactions with oxidizing and/or reducing substances. The result is a transfer of electrons, which causes the position of the Fermi level to shift. The currents between the emitter and the collector change while the voltage at the base remains constant. This allows the detection of these substances (e.g. NH3 gas). **Fig.** 29 shows the schematic architecture of an organic field effect transistors.

[0079] Also conceivable is a combination of an OFET with an OLED. The collector currents of an OFET, which increase in the presence of a substance to be detected, are routed to an OLED. Due to the currents, charge carrier pairs

combine in the luminous layer and electromagnetic radiation is emitted. This allows the conversion of detected gases directly into a light signal.

[0080] Conductive polymers can also be used in batteries. Because they are lighter than metals they offer advantages. These batteries can built up from two differently doped polyacetylene layers. One layer is doped with Li-ions and the other with iodine. A filter paper saturated in polypropylene carbonate and LiClO4 can be used as electrolyte. The architecture of such a battery is shown in **Fig.** 30.

[0081] The inventive adding of pigment substances to the inventive battery achieves the advantage that the conductivity of such polymer battery is maintained over a long period of time. The inventive polymer batteries are also less sensitive to small holes in the layers from which the battery is made. In another embodiment of the inventive batteries, they are colored because of the pigments. The pigmenting substances can be selected such that a color change occurs, preferably as the battery discharges. The user of such battery – without the need for an additional battery charge indicator – is therefore able to recognize based on the color of the battery, if the battery is fully charged or rather close to empty. Here as well, the inventive combination of pigmenting substances and polymer provides a higher mechanical stability in the inventive batteries than the current state of the art is able to provide.

[0082] Another application are electrochemical muscles. The inventive polymers swell when they are doped. This expansion can be used in actuators.

[0083] **Fig.** 31 shows a preferred embodiment of an organic field effect transistor (OFET) **10**. The OFET **10** exhibits a metal substrate **5**. On the metal substrate is an isolator **4**. Positioned on the insulator **4** is the inventive polymer film **3**. Embedded into the polymer film **3** are two conductive layers, drain **1** and source **2**. The substrate **5** serves as gate of the transistor **10**.

[0084] **Fig.** 35 shows an additional embodiment of the invention. In this sample, drain **1** and source **2** are made of different metals. The polymer film **3** is divided into two domains **3a** and **3b** exhibiting different polymers. Thus, a diode is present between **3a** and **3b**. These different domains **3a** and **3b** are created by first polymerizing a specific polymer onto conductors **1** and **2**, and thereafter only onto one of the domains **3a** or **3b** with another monomer – for example, by changing the bath for the polymerization – further polymerized. The change between different polymers can be repeated as often as needed, so that the desired properties of the layer can be adjusted exactly to the requirements. In another embodiment, several polymers are polymerized onto conductors **1** and **2**, which may be designed as interdigital electrodes, for example. Therefore, this embodiment allows measurements between the different polymers. This, too, allows the applicable sensor to be adjusted for a specific sensitivity for a specific gas.

[0085] For the last two embodiments not only the polymers explicitly named in this application can be used but all known polymers. These specifically adjusted layers can be advantageously used as intended by the invention in the food detectors mentioned further above.

[0086] **Fig.** 36 shows an additional sample. Here, a transistor has been created by using for **1** and **2** again different metals while domains **3a**, **3b** and **3c** were doped differently. Domains **3a** and **3c** are p-conductive while domain **3b** is n-conductive.

[0087] **Fig.** 32 shows a layer configuration of an organic photovoltaic cell (solar cell) or of an organic light-emitting diode. Positioned on a transparent glass substrate **11** is a transparent, electrically conductive, organic conductor (e.g. PeDOT) **12** or a transparent electrically conductive inorganic conductor (e.g. ITO). Situated on the organic conductor **12** is the inventive polymer **13**. Deposited onto the polymer again is an organic conductor **14**. In the embodiment according to **Fig.** 32, between layers **12** & **13** and **13** & **14** additional layers of metal, of organic or inorganic semiconductors may be provided.

[0088] **Fig.** 33 shows another preferred embodiment of a component **30** as described in the invention. In this component **30**, located on a glass substrate – which alternatively may be made of metal or plastic – is an electric conductor **22**. Applied to the electric conductor **22** is an inorganic semiconductor. Samples are TiO_2 or SnO_2. Then, located on the inorganic semiconductor **23**, is the inventive polymer **24**. In **Fig.** 33, the surface of the inorganic semiconductor **23** is uneven, so that the polymer film **24** applied to this uneven layer also exhibits an uneven surface **24a**. On surface **24a** may alternatively be a liquid, a gaseous mixture or an electrolyte, wherein the latter may be liquid or solid. This layer of liquid, gaseous mixture or electrolyte is referenced with reference number **25**. This layer **25** is delimited by another layer of an electric conductor **26**. Positioned on the electric conductor **26** is another glass substrate **27**, which alternatively may be made of plastic.

[0089] If the layer **25** is a liquid or a gaseous mixture and if layer **26** is not used, then the component **30** represents a photo-oxidation cell. If the layer **25** is an electrolyte, the component **30** represents a photovoltaic cell, i.e. a solar cell. In this embodiment, the polymer may be bonded to or in the inorganic semiconductor **23**.

[0090] In addition to the embodiments mentioned so far, the inventive polymer film can also be used as semi-permeable membrane for sensor applications.

[0091] **Figs.** 34a and 34e show a schematic view of the base structure of polymers used for the polymerization of the inventive polymer film. These monomers can be used to produce pure polymers as well as copolymers or propfpolymers. The polymerizable group is referenced with the number **31**. Number **32** references the spacer. Number **33** references the organic semiconductor.

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1. Electric component,
with a layer containing at least one polymer affecting the electrical properties of the electric component **characterized in that** the polymer contains at least one molecular organic semiconductor, wherein the at least one molecular organic semiconductor exhibits at least one polymerizable group and wherein the molecular organic semiconductor is polymerized into the polymer via said polymerizable group.

2. Component according to claim 1,
wherein the at least one molecular organic semiconductor includes a macrocyclic ligand and/or its metal complexes, in particular substituted and/or unsubstituted phthalocyanines, substituted and/or unsubstituted porphyrines, substituted and/or unsubstituted porphyrazines, substituted and/or unsubstituted napthalocyanines, substituted and/or unsubstituted biphtalocyanines, substituted and/or unsubstituted merocyanines and/or substituted and/or unsubstituted chlorines,
or a condensed aromatic, in particular substituted and/or unsubstituted perylene dyes and pigments and their derivatives, substituted and/or unsubstituted terrylenes and their derivatives, substituted and/or unsubstituted quaterrylenes and their derivatives, and/or substituted and/or unsubstituted coronenes and their derivatives.

3. Component according to one of the previous claims, wherein the at least one molecular organic semiconductor contains at least one element from the multitude of phthalocyanine, hemiporphyrazine, triazolhemiporphyrazine, biphthalocyanine, naphthalocyanine, phorphyrin, perylene, perylene-dicarbonic acid anhydride, perylene-dicarbonic acid-imide, perylene-tetracarbonic acid dianhydride, perylene-tetracarbonic acid diimide, perylene-tetracarbonic acid monoanhydride monoimide, corones, corone-dicarbonic acid anhydride, corone-dicarbonic acid imide, corone-tetracarbonic acid dianhydride, corone-tetra carbonic acid diimide, corone-tetracarbonic acid monoanhydride-monoimide, rubicen, rubicen dicarbonic acid anhydride, rubicen dicarbonic acid imide, rubicen tetracarbonic acid dianhydride, rubicen tetracarbonic acid-diimide, rubicen-tetracarbonic acid monoanhydride-monoimide, imidazole, imidazole-dicarbonic acid anhydride, imidazole dicarbonic acid imide, imidazole tetracarbonic acid dianhydride, imidazole-tetracarbonic acid diimide, and imidazole-tetracarbonic acid monoanhydride monoimide.

4. Component according to one of the previous claims, wherein the group is polymerizable by electropolymerization.

5. Component according to one of the previous claims, wherein the group contains at least one element of the multitude of aniline, pyrrol, thiophene, ethylene, indole, paraphenylene, aminoanthracene, aminoaphthaline, aminophenol, carbazole, benzoquinone, acrylnitrile, pyrrolidone, phenylenediamine, tetra-thiapentalene, acrylic acid and/or phenol and/ or their derivatives and substituents.

6. Component according to one of the previous claims, wherein the group is bonded to the molecular organic semiconductor via a molecule chain.

7. Component according to claim 6, wherein the molecule chain contains at least one element from the multitude of $(CH.2)_n$, $(CFH)_n$, $(CF_2)_n$, $OCO(CH_2)_n$, $OCO(CF_2)_n$, $OCO(CFH)_n$, $COO(CH_2)_n$, $COO(CF_2)_n$, $COO(CHF)_n$, $NH(CH_2)_n$, $NH(CF_2)_n$, and $NH(CHF)_n$ and/or an aryl moiety, wherein $n = 0$ to 20.

8. Component according to one of the previous claims, wherein the molecular organic semiconductor is modified with at least one additional, non-polymerizable group.

9. Component according to claim 8, wherein the additional group includes at least one element from the multitude of F, Cl, Br, I, CN, OH, SH, CH3 $(CH_2)_nCH3$, phenyl, phenoxy, ethoxy, methoxy, propoxy, iso-propoxy, and tert.-butyl, wherein $n = 0$ to 20.

10. Component according to one of the previous claims, wherein the polymer is electrically conductive.

11. Component according to one of the previous claims, wherein the polymer is doped.

12. Component according to one of the previous claims, with a substrate on which is the film is located, wherein the substrate – preferably in the form of interdigital electrodes – is micro-structured.

13. Component according to claim 12, wherein the substrate is electrically conductive.

14. Component according to one of claims 12 to 13, wherein the film is electropolymerized onto the substrate.

15. Component according to one of the previous claims, wherein the component is a sensor for the measuring of at least the presence, preferably the concentration, of gases and/or liquids in a medium, wherein the film measuring the presence, preferably the concentration, acts as a sensor.

16. Component according to one of the previous claims, wherein the component is an OFET, an OLED, a photovoltaic cell, a Schottky cell, an antistatic film and/or a battery.

17. Method for the manufacture of an electric component with the following steps:
   - an electric conductor is provided,
   - a molecular organic semiconductor is modified with polymerizable groups,
   - the molecular organic semiconductor is electropolymerized onto the electric conductor.

18. Method according to claim 17, wherein consecutively and/or simultaneously different polymerizable groups are utilized.

Attached: 27 Page(s) of drawings

DRAWINGS PAGE 1

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Publication Date: 29 November 2001

CaPc

Li₂Pc

Fig. 1

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Publication Date: 29 November 2001

Fig. 2

α-form

β-form

x-form

○ ··· Zinc
• ··· Nitrogen

Fig. 3

Fig. 4

R_1 = -COOCH$_3$

R_2 = -COOH

Fig. 5

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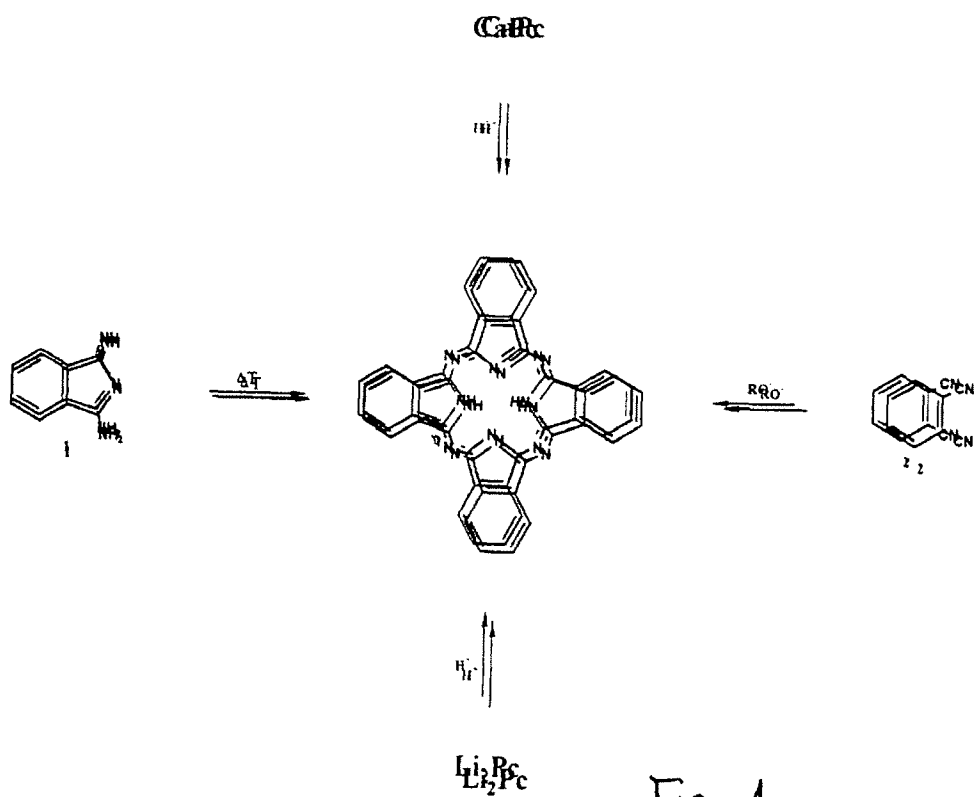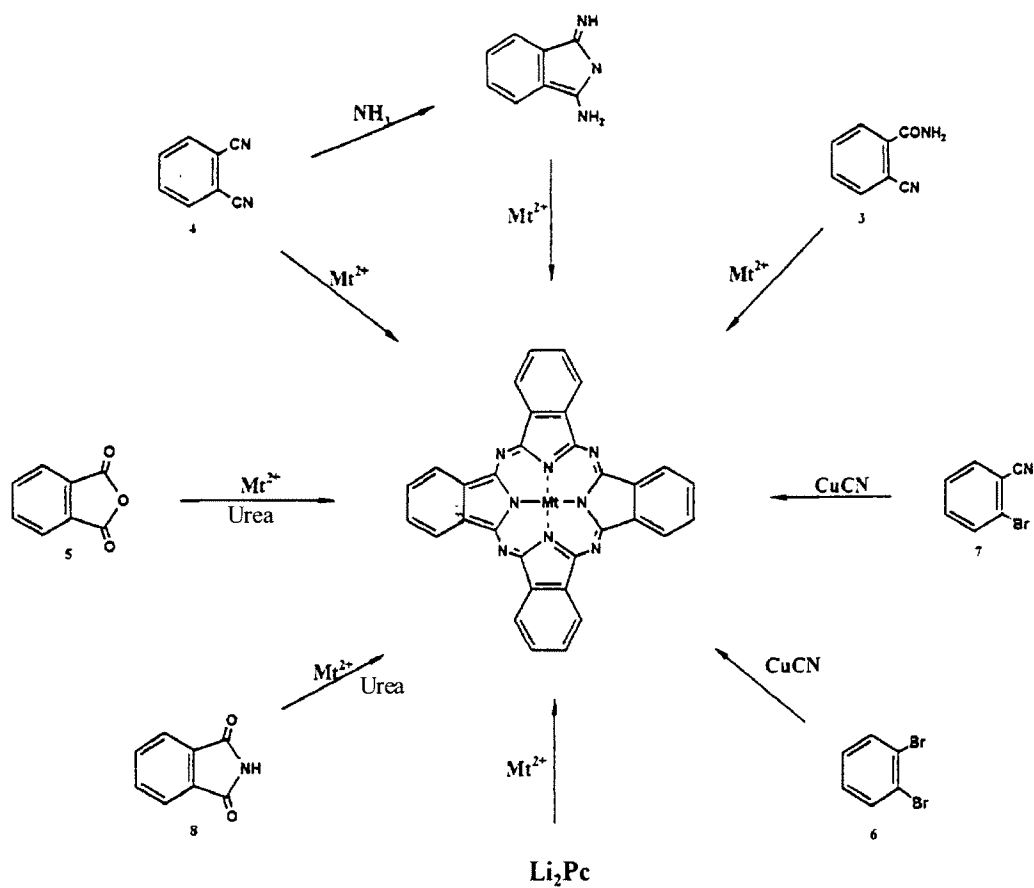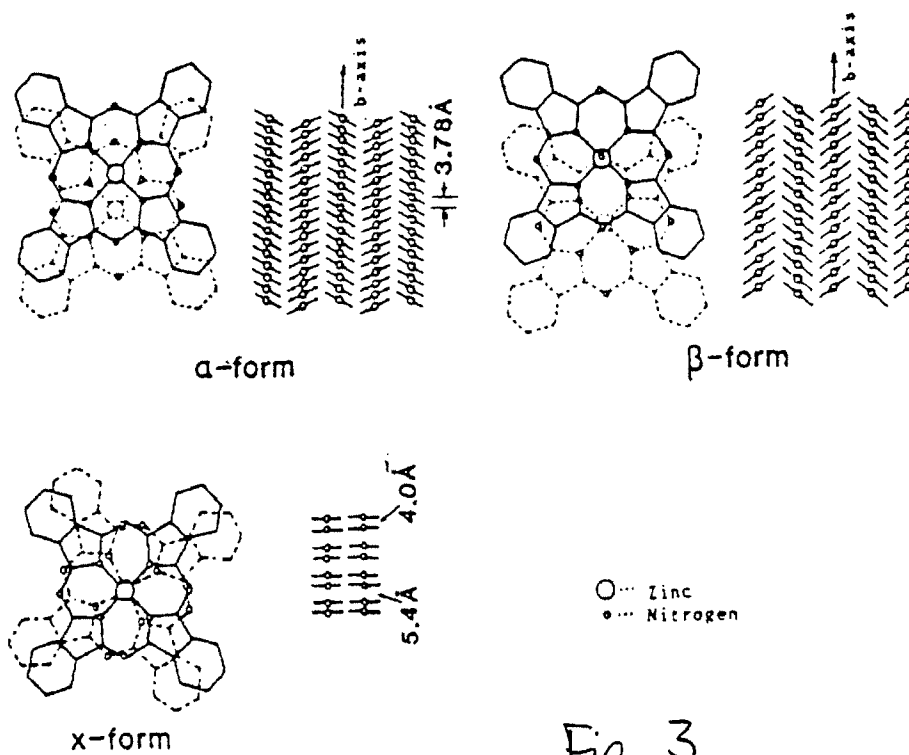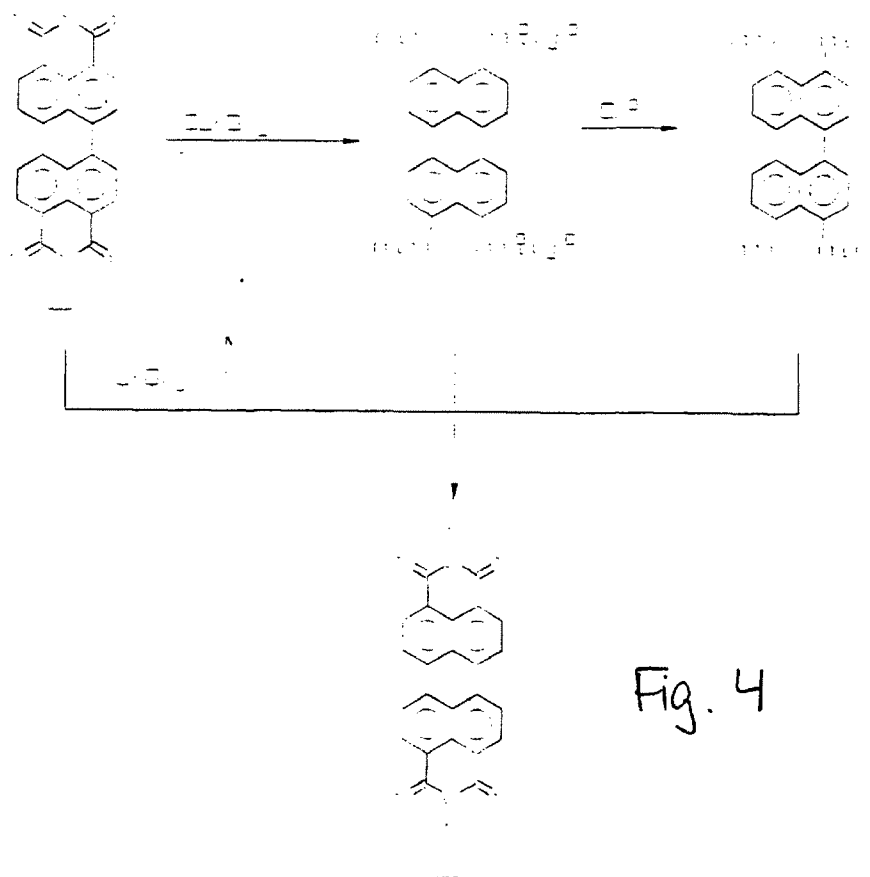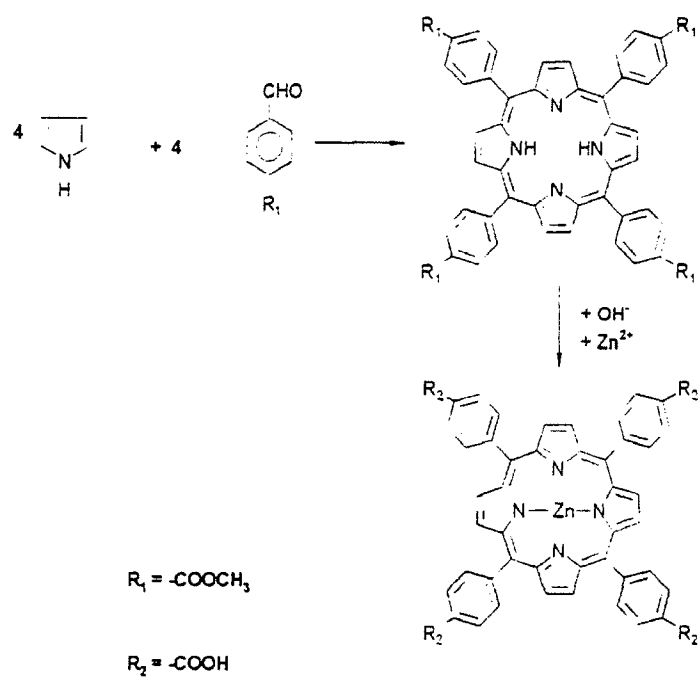
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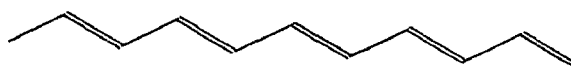
Fig. 6a

Polyphenylene
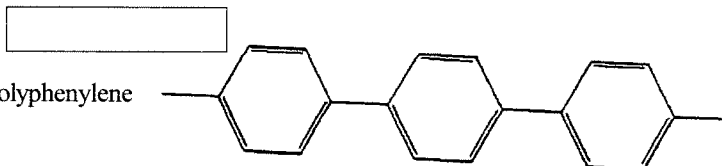
Fig. 6b

Polypyrrol

Fig. 6c

Polyaniline

Fig. 6d

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Fig. 7

Fig. 8

Fig. 9

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Publication Date: 29 November 2001
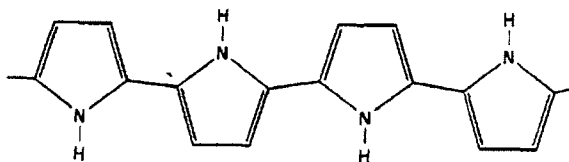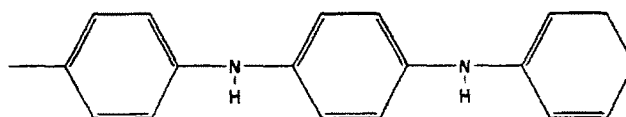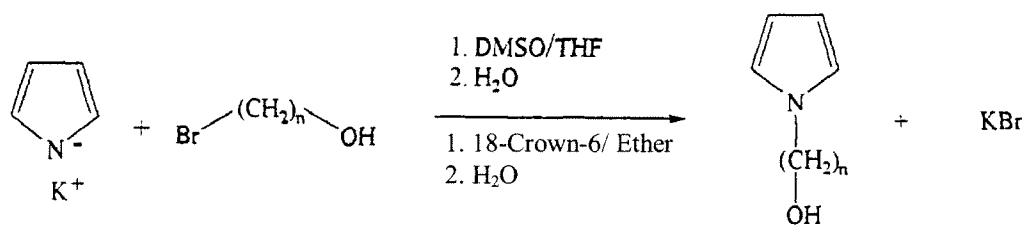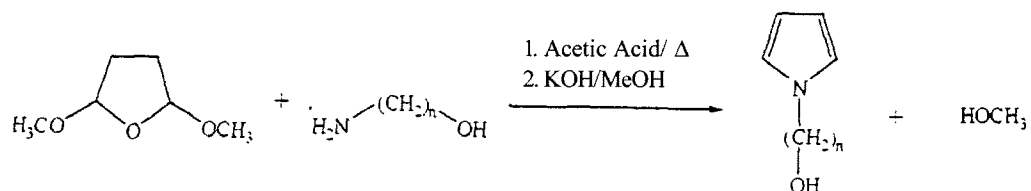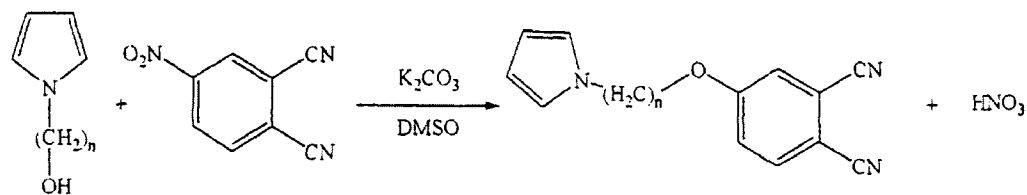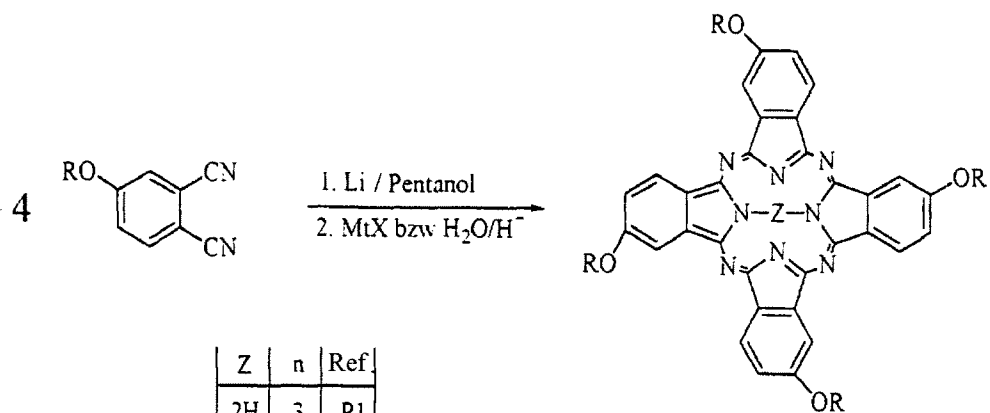
Z	n	Ref.
2H	3	P1
2H	2	P2
Zn	2	P3
Co	2	P4
Ni	2	P5
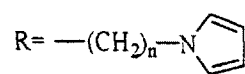
Fig. 10

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$$\xrightarrow[\text{Chlorosulfonic Acid}]{I_2}$$

Fig. 11

$$\xrightarrow[\text{Benzene}]{H_2N-R-NH_2}$$

R	X	Ref.
—⟨⟩—O—⟨⟩—	H	I1
	Cl	I2
—⟨⟩—CH₂—⟨⟩—	H	I3
—⟨⟩—	H	I4
—⟨⟩—	H	I5

Fig. 12

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R	X	Ref
⬡	H	I6
⬡	Cl	I7

Fig. 13

Fig. 14

Fig. 15

Fig. 16

Fig. 17

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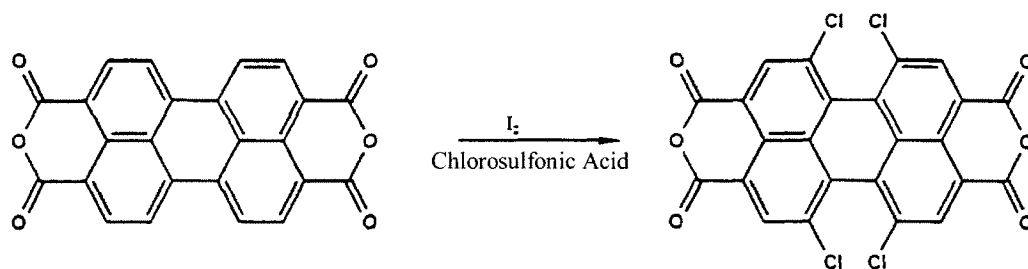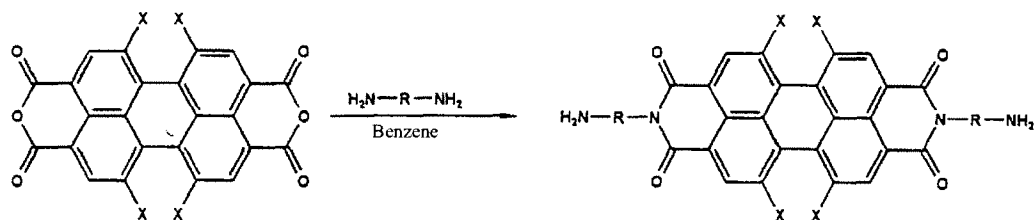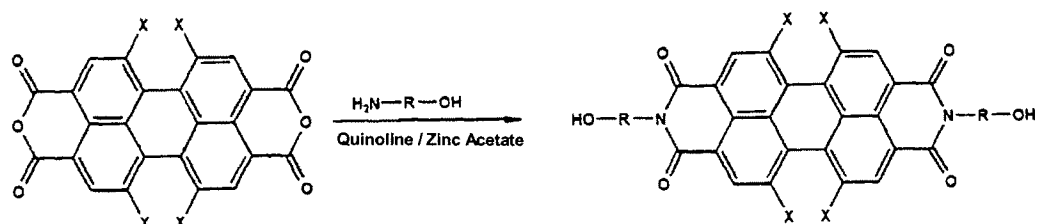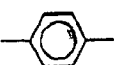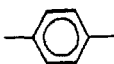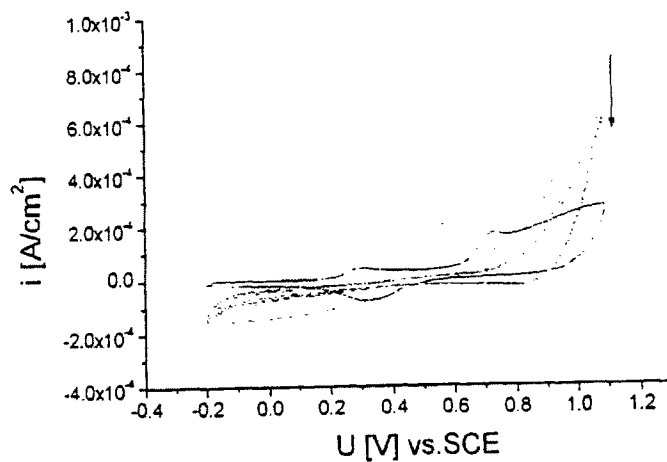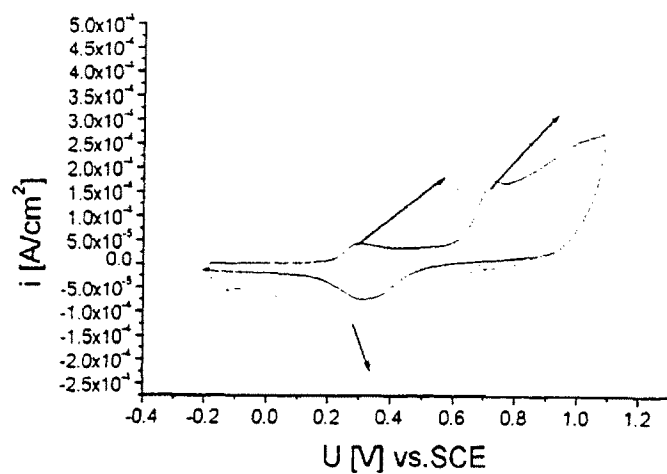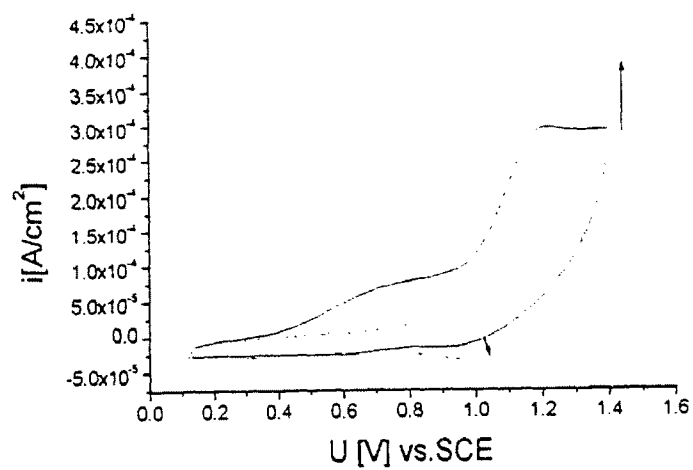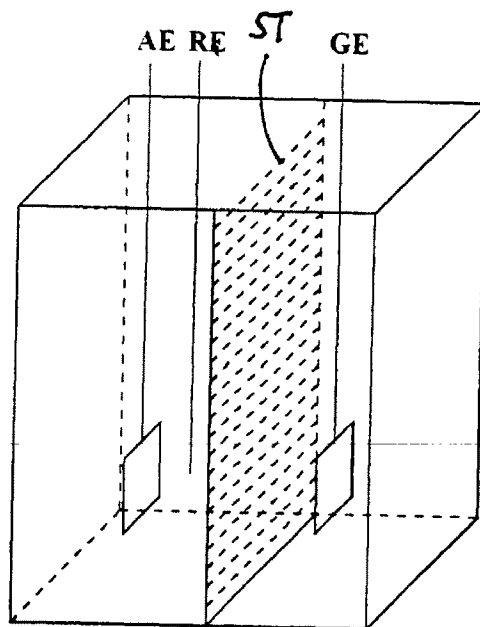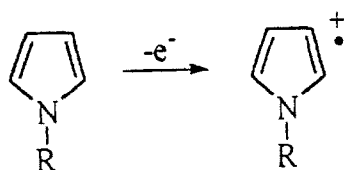
Fig. 18a

Fig. 18b

Fig. 18c

Fig. 18d
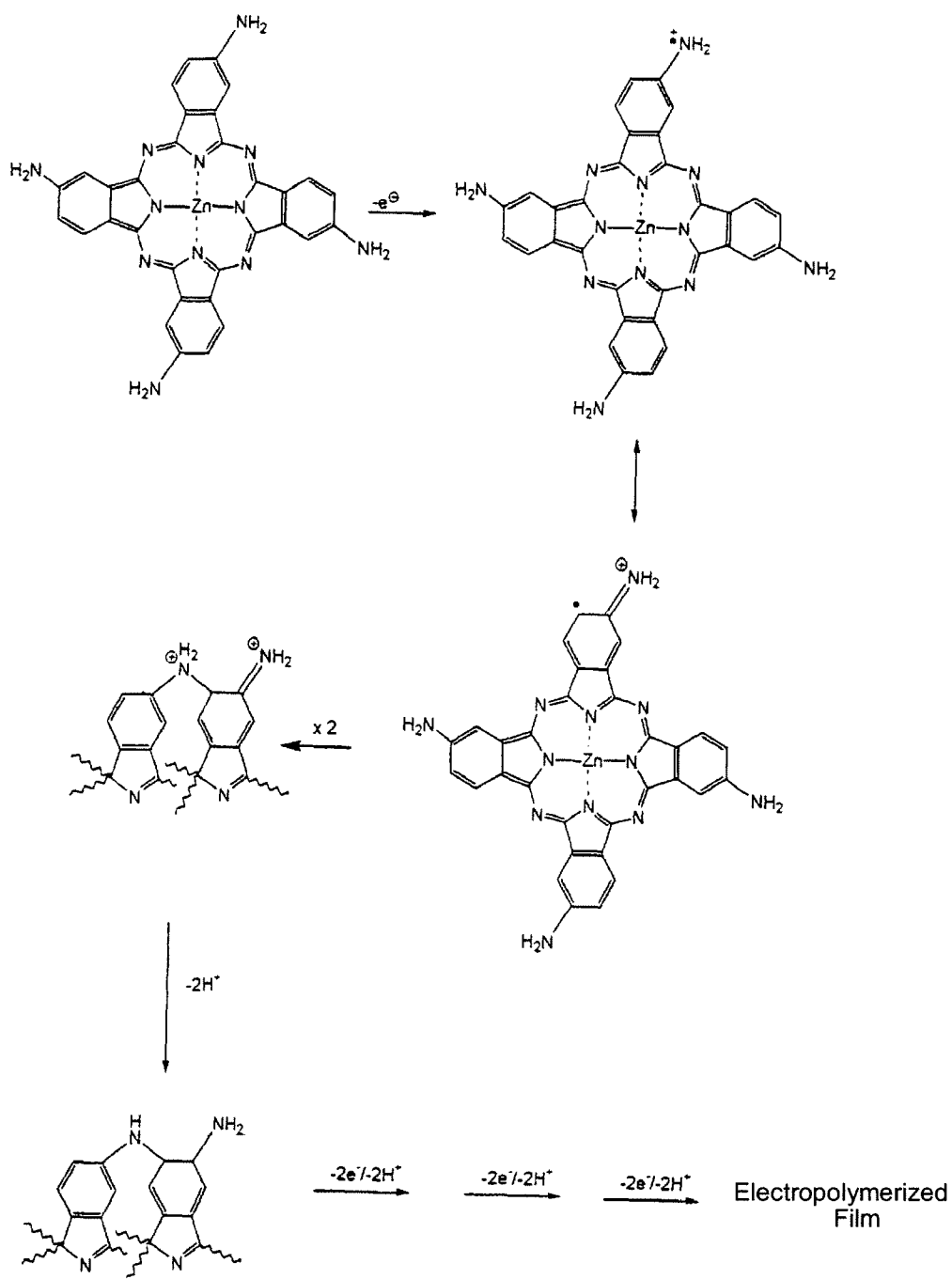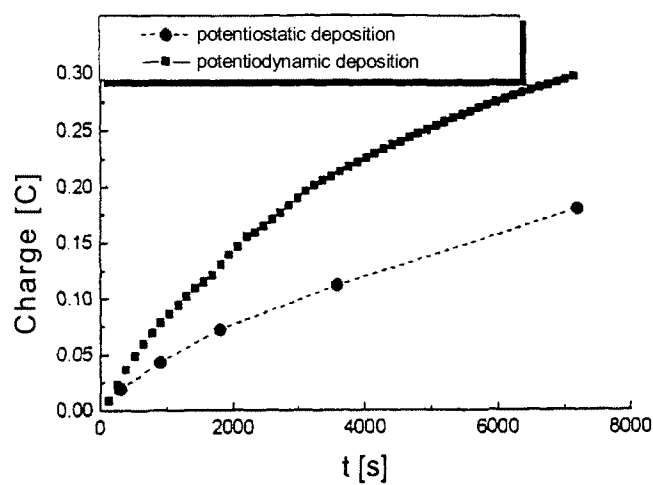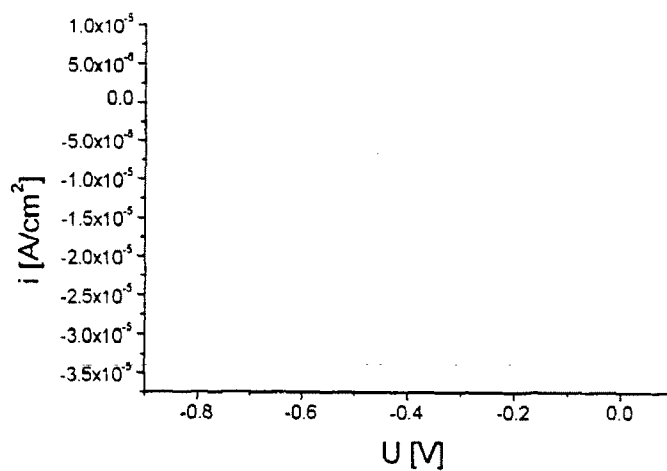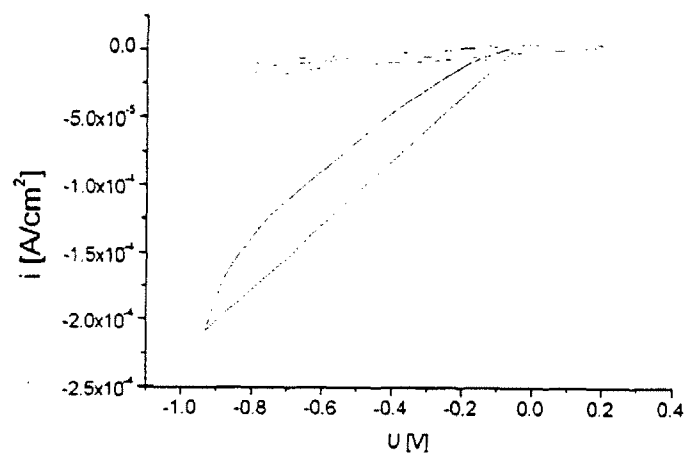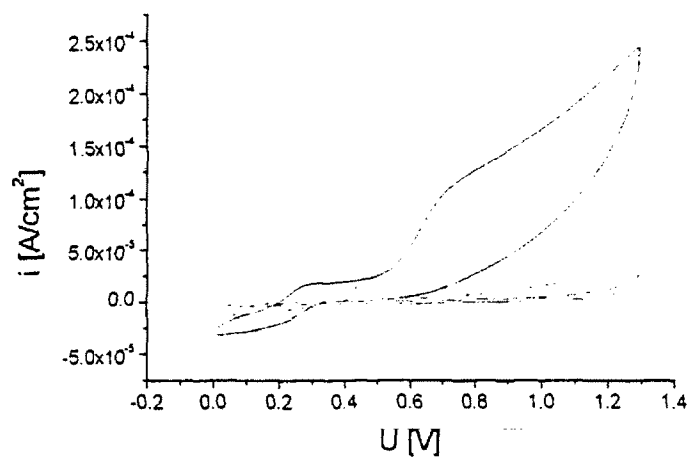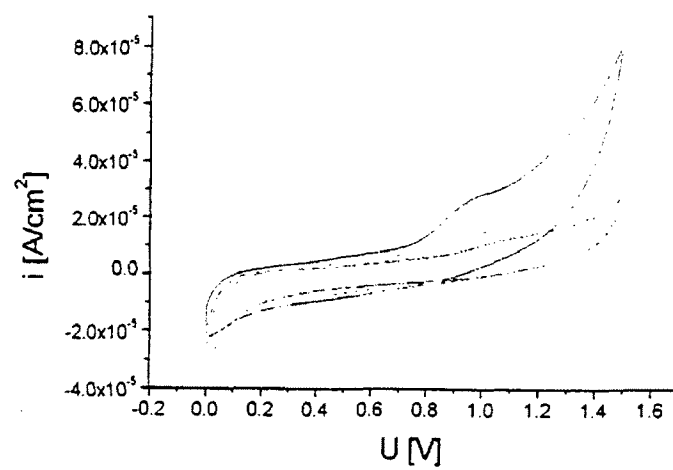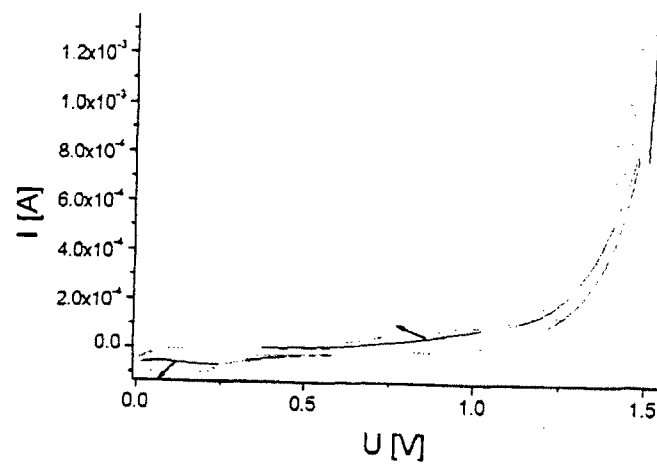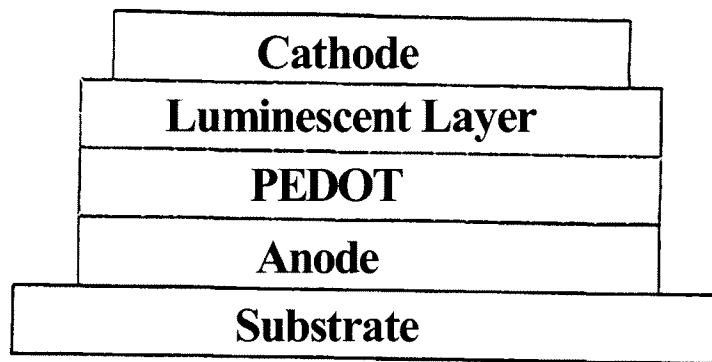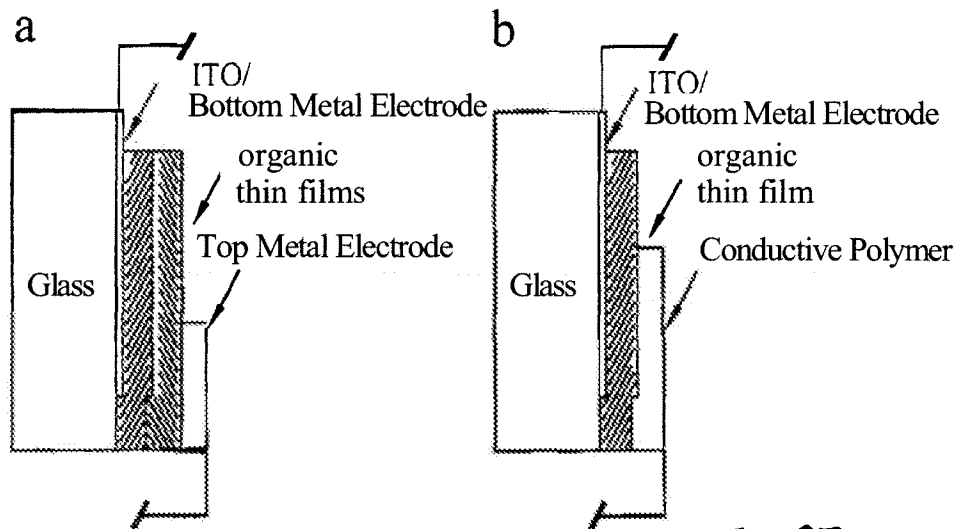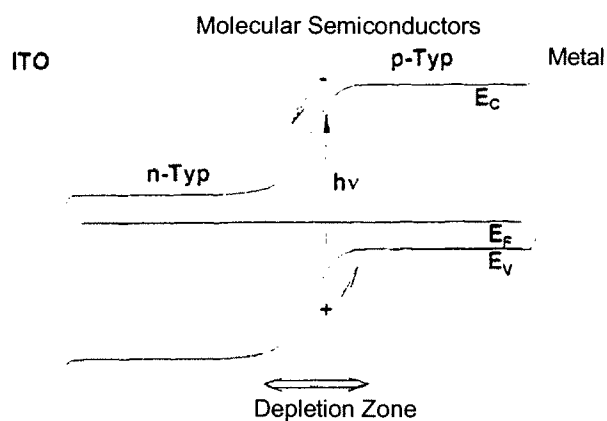
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Fig. 19

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Fig. 20

Fig. 21

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Fig. 22

Fig. 23

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Fig. 24

Fig. 25

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Cathode
Luminescent Layer
PEDOT
Anode
Substrate

Fig. 26

a

ITO/
Bottom Metal Electrode

organic
thin films

Glass

Top Metal Electrode

b

ITO/
Bottom Metal Electrode

organic
thin film

Glass

Conductive Polymer

Fig. 27

Molecular Semiconductors

Fig. 28

Fig. 29

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Charge

Discharge

Fig. 30

Fig. 31

Fig. 32

Fig. 33
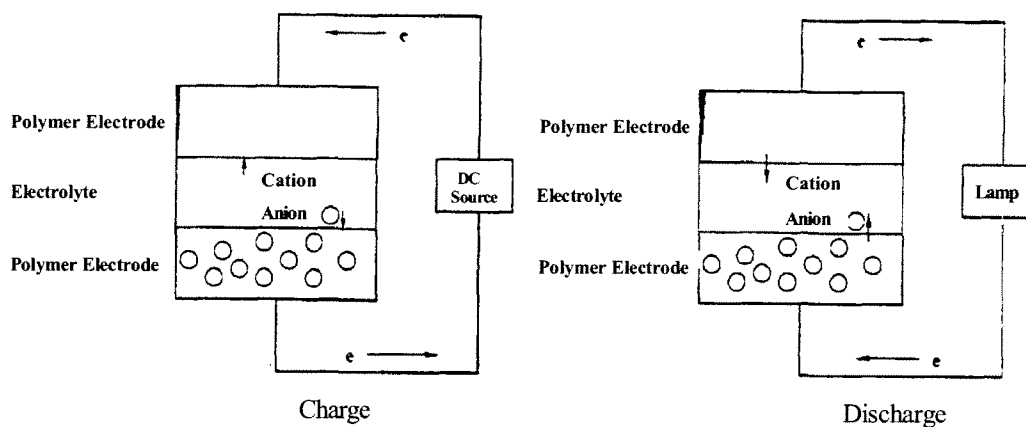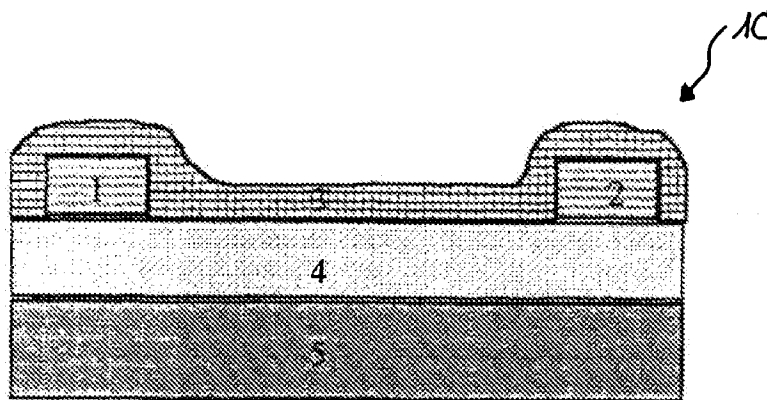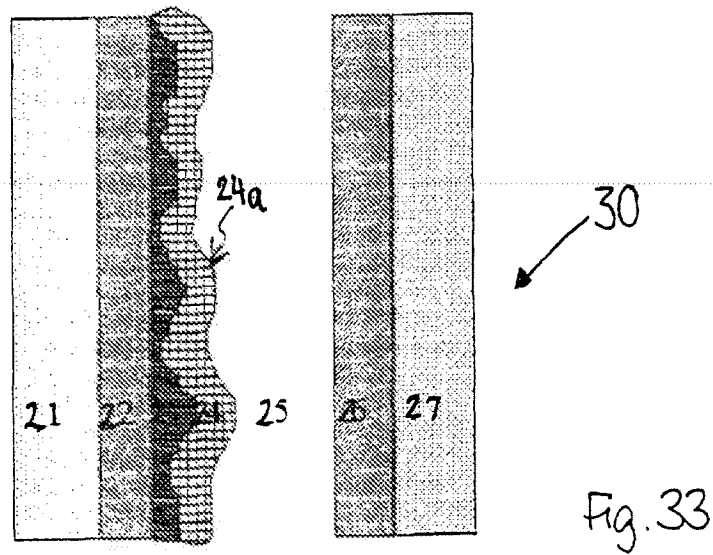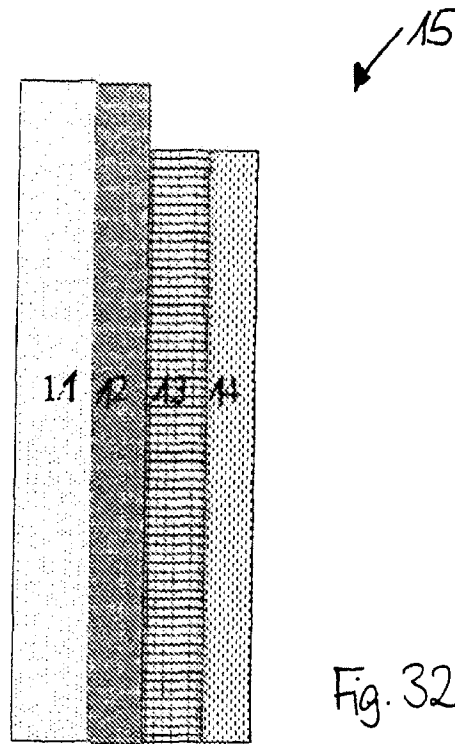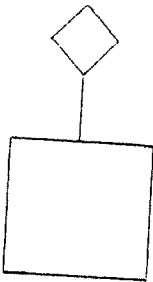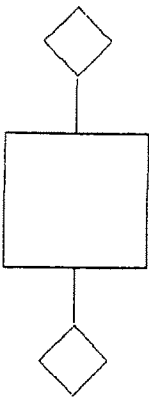
Fig. 34a

Fig. 34b

Fig. 34c

Fig. 34d

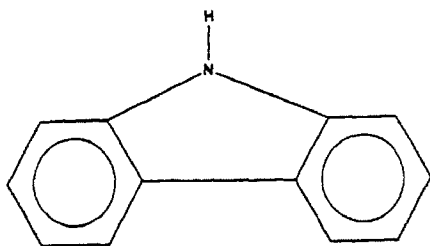Fig. 34e

◇ 31

— 32

□ 33

Fig. 35

Fig. 36

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Fig. 37

Fig. 38

Fig. 39

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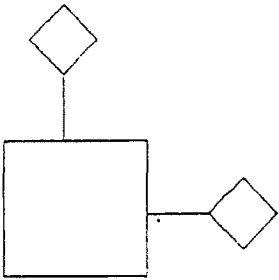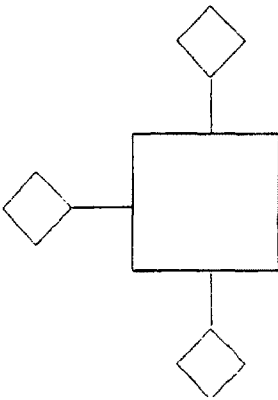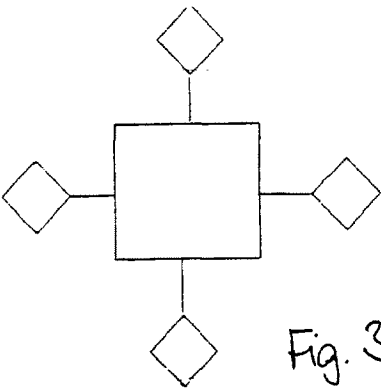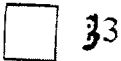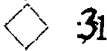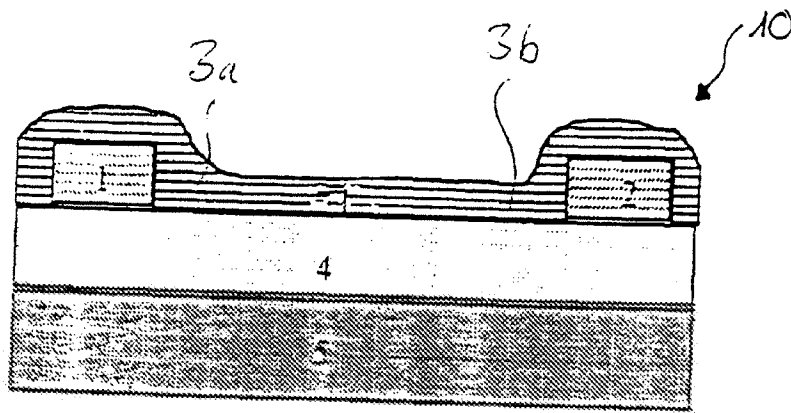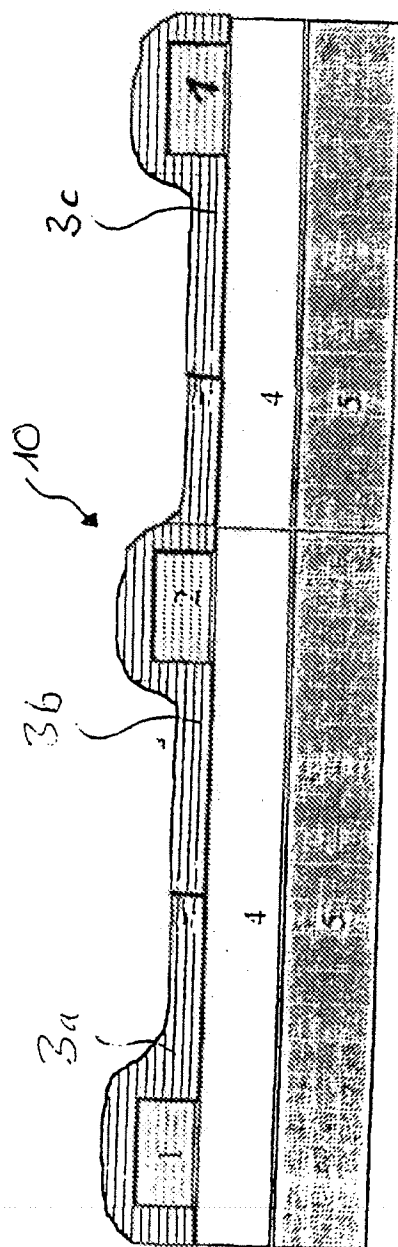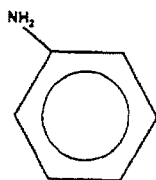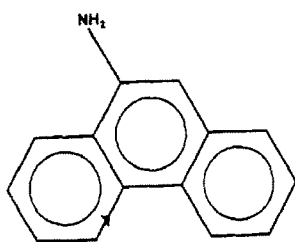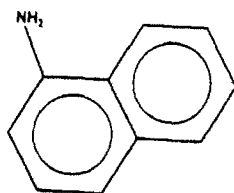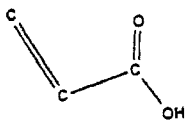
Fig. 40

Fig. 41

Fig. 42

Fig. 43

Fig. 44

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Fig. 45

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